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Technical Challenges of Multipollutant Air Quality Management

Springer

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Foreword

Important changes in air quality management practices are currently underway, especially in the United States and Canada. These changes emphasize (a) improving the efficiency and effectiveness of regulation as it affects human and ecological health, (b) integrating management strategies to minimize risk from multipollutant exposure, and (c) broadening the scope of air quality management to consider the implications of climate change. Because of these changes, the NARSTO Executive Assembly in 2007 directed the NARSTO Management Coordinator to initiate an assessment[1] of the technical challenges facing the atmospheric sciences in implementing risk- and results-based, multipollutant air quality management in North America. The intended audience for the assessment is air quality management decision-makers in Canada, the United States, and Mexico (and especially their technical staffs). However, the assessment also gives an in-depth summary of the technical issues facing contemporary air quality management that should be of interest to air quality professionals outside North America, to non-governmental organizations interested in air quality problems, and to the international academic and research communities, including faculty and students of the atmospheric and environmental sciences.

The formal scope of the assessment and the charge to the assessment team was to:

> …Summarize and assess the scientific resources today and projected over the next five to ten years to address multipollutant options for air quality improvement and consequent improvement in public health and welfare, and ecosystem health, with examples from the energy production and transportation sectors.

and

> …provide a state-of-science evaluation that gives a critical summary of the opportunities, limitations and information gaps over the projected ten year horizon, giving insight into the development of mulipollutant management strategies. The evaluation will account for

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[1] Three previous assessments have been prepared by NARSTO: An Assessment of Tropospheric Ozone (NARSTO 2000); Particulate Matter Science for Policy Makers (NARSTO 2004); and Improving Emission Inventories for Effective Air Quality Management Across North America (NARSTO 2007).

> measuring improvement in human health and welfare and ecosystem health using a multimedia framework and incorporating a climate change-air quality linkage. Similarities and differences in approach encompassing North American nations are to be considered in developing the relevant knowledge accessible to decision-makers.

In addressing the NARSTO charge, the assessment team considered the current science available to comprehensively address risk- and results-based multipollutant air quality management. To identify where scientific information gaps might lie, the team proposed a conceptual framework for multipollutant air quality management, including the driving priorities for reducing health and ecological effects. This effort resulted in a critical summary of the opportunities for and limitations of multipollutant air quality management, and the information gaps that would need to be filled over the next ten years in order to advance a risk- and results-based multipollutant management approach.

Our study derives from and extends the U.S. National Research Council (2004) report *Air Quality Management in the United States*, which advocated a more integrated and comprehensive approach to air quality management that focuses on controlling pollutant emissions that pose the most significant risks. Although there has been significant progress in improving air quality in all three countries of North America, this progress has been achieved following a largely individual-pollutant approach to air quality management that is driven by the need to meet individual ambient concentration standards. Although it may have been successful in the past, the NRC report argues that this approach possesses inherent limitations that constrain its ability to meet important future challenges such as increasingly stricter standards, the health effects of exposure to air toxics, the apparent absence of a risk threshold for most pollutants, environmental justice issues, ecosystem effects, long-range transport, and climate change.

Because NARSTO's primary competence lies in the atmospheric sciences, this assessment focuses principally on these scientific elements. However, the ultimate goal of air quality management is to protect human health and vulnerable ecosystems; thus, air quality control measures must be accountable not only for reducing emissions and the ambient concentrations of pollutants, but also in protecting human and ecosystem health. The assessment, therefore, includes reviews of the effects of air pollution on health and ecosystem functions and on the information atmospheric science must provide health and ecosystem scientists to enable them to understand and assess these effects.

This assessment was prepared under the oversight of an executive subcommmittee named by the NARSTO Executive Steering Committee. The subcommittee members are: Howard Feldman (American Petroleum Institute), John Jansen (Southern Company Services, Inc.), Naresh Kumar (EPRI), Keith Puckett (Environment Canada), James Vickery (U.S. Environmental Protection Agency [now retired]), Timothy Watkins (U.S. Environmental Protection Agency), and Susan Wierman (Mid-Atlantic Regional Air Management Association [MARAMA]). The co-chairs of the report are: Jeff Brook (Environment Canada), Kenneth Demerjian (State University of New York at Albany), George Hidy (Envair/Aerochem), Luisa Molina (Massachusetts Institute of Technology and the Molina Center for Energy and the Environment), and Richard Scheffe (U.S. Environmental Protection Agency).

The content of the assessment was written by subject matter experts from Canada, the United States, and Mexico. In addition to the co-chairs, the principal authors and contributors to the assessment are listed in the List of Contributors and Acknowledgments.

Appendices, available as PDF files from the NARSTO web site (www.narsto.org), contain additional technical detail, particularly in reference to examples of risk analysis and aerometric measurements in North America.

Many others supported the preparation of this assessment. First and foremost, completion of this assessment would not have been possible without the leadership provided by George Hidy. Thanks go to William Pennell as NARSTO Management Coordinator for his administrative oversight and technical contributions, and to Jeff West as NARSTO Associate Management Coordinator for his technical and administrative efforts. Our sincere appreciation goes to Betsy Owczarski, our technical editor, and to Diane Fleshman, our administrative assistant. We also acknowledge the assistance of Devary Communications, Richland Washington, in preparing the final versions of the graphics. Without them, the report could not have been completed. Our thanks go to investigators in Environment Canada, the Ontario Ministry of Environment, Instituto Nacional de Ecologia of Mexico, the U.S. Environmental Protection Agency, EPRI, and Southern Company Services, Inc. Thanks also go the Oak Ridge Institute for Science and Education for assistance in facilitating meetings and interactions with the contributors.

The draft report was reviewed by the NARSTO oversight subcommittee and NARSTO member representatives. The assessment draft was externally peer reviewed by Don McKay, chair (Environment Canada, retired), Charles Driscoll (Syracuse University), Daniel Greenbaum (Health Effects Institute), John Watson (the Desert Research Institute), and Steve Ziman (Chevron Corporation, retired).

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Disclaimer

The views expressed in this assessment are those of the authors and do not necessarily reflect the views or policies of any organization within or outside of the NARSTO community. Further, any policy implications derived from the material herein cannot be considered to be endorsed by NARSTO or its member organizations.

Preface

In 2007, NARSTO[1] was asked to assess the technical challenges of transitioning from an individual pollutant approach to air quality management to a risk-based approach that (a) includes integrated consideration of all pollutants that pose significant risks to human health and ecosystem function and (b) provides the information needed to assess the effectiveness of actions that might be taken to reduce these risks. This assessment was undertaken in response to a 2004 U.S. National Research Council (NRC) report: *Air Quality Management in the United States* (The National Academies Press, Washington, D.C.).

Air quality management in Canada, the United States, and Mexico has been successful in reducing air pollution, especially in urban areas. However, the 2004 NRC report concluded that the air quality management system in the United States, and presumably in other countries as well, contains inherent limitations that constrain its ability to meet future challenges such as increasingly stricter standards, the health effects of exposure to air toxics, the apparent absence of a risk threshold for most pollutants, environmental justice issues, ecosystem effects, long-range transport, and climate change.

To address these challenges, the NRC recommended that current air quality management approaches that tend to focus on independent attainment of separate air quality management standards be transformed to an approach that strives to

- Identify and assess more clearly the most significant exposures, risks, and uncertainties.
- Take an integrated multipollutant approach to controlling emissions of pollutants posing the most significant risks.
- Take an airshed-based approach by assessing and controlling emissions of important pollutants arising from local, multistate, national, and international sources.
- Emphasize results over process, create accountability for the results, and dynamically adjust and correct the system as data on progress are assessed.

This book takes a comprehensive look at how close we are to having the information and tools needed to achieve this vision. It provides comprehensive reviews of

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[1] NARSTO (formerly the North American Research Strategy for Tropospheric Ozone) is a collaboration among government agencies, the private sector, and academia in Canada, the United States, and Mexico that is dedicated to advancing the scientific foundations of air quality management in North America.

current risk assessment methodologies, environmental and emission information, air quality measurements, modeling, and the underlying knowledge that supports risk assessment and evaluation of the effectiveness of air quality management policies. We also address the problem of how global-scale changes in emissions and changes in climate will affect future air quality management. The book reviews how closely past air quality management actions have approached the above-stated NRC vision, and it concludes with recommendations on how a transition to an approach that fulfills this vision might be facilitated.

We conclude that there are theoretical advantages to an integrated risk-based approach, but note that achieving it will be an evolutionary process. This evolution will require improvements in the discipline of exposure assessment and in our understanding of the consequences to human and ecosystem health of simultaneous exposure to multiple pollutants. It will require changes in monitoring approaches to support risk assessments, and it will require considerable advance planning to select the appropriate metrics for evaluating air quality management actions and to obtain the information needed to support these metrics.

August 2010 William T. Pennell
NARSTO Management Coordinator,
Pasco, Washington

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List of Terms

Accountability	A formal iterative process evaluating the effect of air quality management actions on emissions, ambient air, receptor exposure, human health and welfare, and ecosystem protection. The process uses measurements and models to describe trends in key indicators and cause-effect associations across a source to effects continuum. The process uses initial forecasts of regulatory impact to gauge performance. The outcome of the process infers the results of management considerations and actions, diagnoses possible shortfalls, and identifies new courses of action.
Air Pollutant	Any substance in air that could, in high enough concentration, harm humans, other animals, vegetation or material. Pollutants may include almost any airborne material of manmade origin or natural material modified by man's activities. They may be in the form of gases, solid or liquid particles or a combination thereof. Generally pollutants fall into two classes: (1) those emitted directly from identifiable sources and (2) those produced in the air by interaction between two or more emitted pollutants, or by physicochemical reaction with normal atmospheric constituents, with or without photo-activation (http://www.nsc.org/ehc/glossary.html).
Airborne Toxins	Trace chemicals found both in source emissions, workplace air and in ambient air with the potential for catalyzing certain respiratory, neurotoxic or other diseases, including cancer. In the United States, these are designated in ambient air as hazardous air pollutants (HAPs). There are 187 HAPs, including metals, organics and certain generics like coke oven emissions, listed in the U.S. Clean Air Act (Table A); most of these are of concern in Canada (Table B) and Mexico (Table C) as well. For purposes of this report, airborne toxins are referred to as air toxics or HAPs.

Climate Forcing Pollutants	Air pollutants that contribute to climate forcing or interference through modification of the earth's radiation balance. These pollutants include carbon dioxide (CO_2), ozone (O_3), nitrous oxide (N_2O), certain chlorofluorocarbons (CFCs) and fine particles.
Dose	The amount of mass of a pollutant which reaches a specific target organ in humans over a given period of time.
Exposure	Humans and ecosystem components reside in the atmosphere and as a result encounter contaminants in the air. Exposure involves contact of a stressor (e.g., an air pollutant) with a receptor (human or ecosystem). Exposure is often identified with pollutant concentrations, and may occur outdoors, indoors, or during periods of different activity. Human exposure is measured in terms of spatial and temporal variations of ambient air concentrations, indoor air concentrations, including infiltration of ambient air, and activity patterns of individuals or estimated population averages. Ecosystem components include vegetation, wildlife, soils, natural waters, and aquatic biota. Exposure for ecosystem components is identified by their contact with ambient air. Pollution regulation focuses on the exposure component from ambient (outdoor) air.
Health Effects	Effects on human health induced by exposure to airborne contaminants potentially attributed to physicochemical and biological mechanisms. Measures of adverse effects are used in individual or community (epidemiologic) studies, many of which relate to respiratory or cardiovascular responses. Laboratory (toxicological) studies have adopted a number of measures of response in *in-vitro* or *in-vivo* conditions that complement those used in epidemiology.
High Volume Pollutants	Gaseous or condensed-phase contaminants emitted at a high volume rate; they are found in ambient air in concentrations of multiple parts per billion or multiple $\mu g/m^3$. The U.S.-defined Criteria Pollutants—carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides ($NO+NO_2$, stated as NO_2), ozone (O_3), particulate matter (PM) are high volume pollutants. (In the United States, lead is also a Criteria Pollutant, though it is not emitted at high volume; lead also is designated a HAP.)
Multiple Media	Ambient air, terrestrial and water systems that are integrated through atmospheric exposure or deposition.

Multipollutant Air Quality Management	Air quality planning and implementation addressing groups of pollutants having common or intermingled sources, similar precursors or products of atmospheric chemical reactions, common biological receptors, or common effects in humans or ecosystems. The objective is an integrated approach to emission reduction strategies, accounting for all regulated emissions and technologies, to maximize air quality improvement and environmental protection in an efficient manner, while minimizing unintended consequences of change.
Risk-Based Air Quality Management	Development and implementation of an air quality management strategy that addresses by priority and optimization the risk reduction in human health and welfare, and ecosystems incurred by exposure reduction to air pollutants, using short and long term impacts.
Single Pollutant Air Quality Management	Air quality planning and implementation of individual, designated criteria pollutants and HAPs in accordance with the requirements of national policies, with emphasis on meeting air quality goals for ambient air quality or levels of emissions.

Table A Hazardous air pollutants list (1990 U.S. EPA Clean Air Act Amendments)[a]

- Acetaldehyde[b]
- Acetamide
- Acetonitrile
- Acetophenone
- 2-Acetylaminofluorene
- Acrolein*[b]
- Acrylamide
- Acrylic acid
- Acrylonitrile[b]
- Allyl chloride
- 4-Aminobiphenyl
- Aniline
- o-Anisidine
- Asbestos*
- Benzene (including benzene from gasoline)*[b]
- Benzidine
- Benzotrichloride
- Benzyl chloride
- Biphenyl
- Bis (2-ethylhexyl)phthalate (DEHP)
- Bis(chloromethyl)ether*
- Bromoform
- 1,3-Butadiene*[b]
- Calcium cyanamide
- Caprolactam[c]
- Captan
- Carbaryl
- Carbon disulfide
- Carbon tetrachloride*[b]
- Carbonyl sulfide
- Catechol
- Chloramben
- Chlordane
- Chlorine
- Chloroacetic acid
- 2-Chloroacetophenone
- Chlorobenzene
- Chlorobenzilate
- Chloroform[b]
- Chloromethyl methyl ether
- Chloroprene
- Cresols/cresylic acid (isomers and mixture)
  - o-Cresol
  - m-Cresol
  - p-Cresol
- Cumene
- 2,4-D, salts and esters
- DDE
- Diazomethane
- Dibenzofurans
- 1,2-Dibromo-3-chloropropane
- Dibutylphthalate
- 1,4-Dichlorobenzene(p)
- 3,3-Dichlorobenzidene
- Dichloroethyl ether (Bis (2-chloroethyl)ether)
- 1,3-Dichloropropene[b]
- Dichlorvos
- Diethanolamine
- N,N-Diethyl aniline (N,N-Dimethylaniline)
- Diethyl sulfate
- 3,3″-Dimethoxybenzidine
- p-Dimethyl aminobenzene
- 3,3′-Dimethyl benzedine
- Dimethyl carbamoyl chloride
- N, N-Dimethyl formamide
- 1,1-Dimethyl hydrazine
- Dimethyl phthalate
- Dimethyl sulfate
- 4,6-Dinitro-o-cresol, and salts
- 2,4-Dinitrophenol
- 2,4-Dinitrotoluene
- 1,4-Dioxane (1,4-Diethyleneoxide)
- 1,2-Diphenylhydrazine
- Epichlorohydrin (l-Chloro-2,3-epoxypropane)
- 1,2-Epoxybutane
- Ethyl acrylate
- Ethyl benzene
- Ethyl carbamate (Urethane)
- Ethyl chloride (Chloroethane)
- Ethylene dibromide[b] (Dibromoethane)
- Ethylene dichloride[b] (1,2-Dichloroethane)
- Ethylene glycol
- Ethylene imine (Aziridine)
- Ethylene oxide*[b]
- Ethylene thiourea
- Ethylidene dichloride (1,1-Dichloroethane)[b]
- Formaldehyde*[b]
- Heptachlor
- Hexachlorobenzene*[b]
- Hexachlorobutadiene*
- Hexachlorocyclopentadiene
- Hexachloroethane
- Hexamethylene-1,6-diisocyanate
- Hexamethylphosphoramide
- Hexane
- Hydrozine[b]
- Hydrochloric acid
- Hydrogen fluoride* (Hydrofluoric acid)
- Hydrogen sulfide[c]
- Hydroquinone
- Isophorone
- Lindane (all isomers)
- Maleic anhydride
- Methanol
- Methoxychlor
- Methyl bromide* (Bromomethane)
- Methyl chloride* (Chloromethane)
- Methyl chloroform* (1,1,1-Trichloroethane)
- Methyl ethyl ketone (2-Butanone)[c]
- Methyl hydrazine
- Methyl iodide (Iodomethane)
- Methyl isobutyl ketone (Hexone)
- Methyl isocyanate
- Methyl methacrylate
- Methyl tert-butyl ether
- 4,4-Methylene bis(2-chloroaniline)
- Methylene chloride[b] (Dichloromethane)
- 4,4′-Methylene diphenyl diisocyanate (MDI)
- 4,4-Methylenedianiline
- Naphthalene
- Nitrobenzene
- 4-Nitrobiphenyl
- 4-Nitrophenol
- 2-Nitropropane
- N-Nitroso-N-methylurea
- N-nitrosodimethylamine*
- N-nitrosomorpholine
- Parathion
- Pentachloronitrobenzene (Quintobenzene)
- Pentachlorophenol
- Phenol
- p-Phenylenediamine
- Phosgene
- Phosphine
- Phosphorus
- Phthalic anhydride
- Polychlorinated biphenyls (Aroclors)*[b]
- 1,3-Propane sultone
- beta-Propiolactone
- Propionaldehyde
- Propoxur (Baygon)
- Propylene dichloride[b] (1,2-Dichloropropane)
- Propylene oxide

Table A (continued)

1,2-Propylenimine (2-Methyl aziridine)
Quinoline[b]
Quinone
Styrene
Styrene oxide
2,3,7,8-Tetrachlorodibenzo-p-dioxin*
1,1,2,2-Tetrachloroethane
Tetrachloroethylene* (Perchloroethylene)
Titanium tetrachloride
Toluene*
2,4-Toluene diamine
2,4-Toluene diisocyanate
o-Toluidine
Toxaphene (chlorinated camphene)
1,2,4-Trichlorobenzene
1,1,2-Trichloroethane*
Trichloroethylene*
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triethylamine
Trifluralin
2,2,4-Trimethylpentane
Vinyl acetate
Vinyl bromide
Vinyl chloride*[b]
Vinylidene chloride (1,1-Dichloroethylene)
Xylenes (isomers and mixture)*
  o-Xylenes
  m-Xylenes
  p-Xylenes
Antimony compounds
Arsenic*[b] compounds (inorganic including arsine)*
Beryllium compounds[b]
Cadmium compounds*[b]
Chromium compounds*[b]
Cobalt compounds
Coke oven emissions[b]
Cyanide compounds[d]
Glycol ethers[e]
Lead compounds*
Manganese compounds*[b]
Mercury compounds*[b]
Fine mineral fibers[f]
Nickel compounds*[b]
Polycylic organic matter[g], *[b]
Radionuclides (including radon)[h]
Selenium compounds

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[a] Note the asterisks are those HAPs that are listed in Canada as toxic species under CEPA (EC 2008). Toluene and xylenes are included as ‘fuel containing toxic substances’ in CEPA. For a complete list of Canadian and Mexican air toxics, see Tables B and C

[b] High priority designation for U.S. National Air Toxics Assessment

[c] Removed from original list of 188 for details see (http://www.epa.gov/ttn/atw/pollutants/atwsmod.html)

Note for all listings above which contain the word “compounds” and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical’s infrastructure

[d] X′CN where X = H′ or any other group where a formal dissociation may occur. For example KCN or $Ca(CN)_2$

[e] Includes mono- and di ethers of ethylene glycol, diethylene glycol, and triethylene glycol $R–(OCH_2CH_2)_n–OR'$ where n = 1, 2, or 3; R = alkyl or aryl groups; R′ = R, H, or groups which, when removed, yield glycol ethers with the structure: $R–(OCH_2CH)_n–OH$. Polymers are excluded from the glycol category

[f] Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less

[g] Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C

[h] A type of atom which spontaneously undergoes radioactive decay

Table B Air toxic list schedule 1 Canadian Environmental Protection Act of 1999[a]

Chlorobiphenols
Dodecachloopentacyclodecane (Mirex)
Chlorofluorcarbons
Asbestos
Lead
Mercury
Vinyl chloride
Bromochloromethane
Bromochlorodifluoromethane
Dibromotetrafluoroethane
Fuel containing toxic substances
Dibenzo-para-dioxin
Dibenzofuran
Polychlorinated dibenzo-para-dioxins
Polychlorinated dibenzofurans
Tetrachlormethane (carbon tetrachloride)
1,1,1-trichloroethane
Bromofluorocarbons
Hydrobromofluorocarbons
Methyl bromide
Bis(chloromethyl) ether
Chloromethyl, ethyl ether
Hydrochlorofluorocarbons
Benzene
Inorganic arsenic compounds
Inorganic cadmium compounds
Hexavalent chromium compounds
1,2-dichlorbenzene
Inorganic fluorides
Oxidic, sulphidic and soluble inorganic nickel compounds
Polycyclic aromatic hydrocarbons
Tetrachloroethylene
Trichloroethylene
Bromochloromethane
Acetaldehyde
1,3-butadiene
Acrylonitrile
Respirable particulate matter <10 μm
Acrolein
Ethylene oxide
Formaldehyde
N-Nitrosodimethylamine
Gaseous ammonia
Ozone
Nitric Oxide
Nitrogen Dioxide
Sulphur Dioxide
Volatile organic compounds
Hexachlorobutadiene
Particulate matter containing metals release from copper smelting and refining
Particulate matter containing metals from zinc plants

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[a] The Canadian Environmental Protection Act of 1999, CEPA (1999), Schedule 1 has designated 85 air toxic species listed in Table TB6.1a. Many of these species share similar classifications to those listed under U.S. air toxics and hazardous air pollutants, but several listed are identified as criteria pollutants (e.g., O_3, NO, NO_2, SO_2) in the U.S. In addition, there are other designated species which are not listed in the U.S. and representative of aggregated classes of compounds (e.g., particulate matter containing metals released from copper smelting and refining or particulate matter containing metals from zinc plants). As some species listed are semi-volatile, while others are non-volatile at ambient temperatures, the species may be present in aerosol form depending on ambient conditions (See http://www.ec.gc.ca/CEPARegistry/subs_list/Toxicupdate.cfm)

Table C Air toxics surveyed in the Valley of Mexico[a]

Toluene[*]
Methanol[*]
1,1,1,-trichloroethane[*]
Xylenes[*]
n-hexane[*]
Methyltributylether
Trichloroethylene[*]
Benzene[*]
m-xylene[*]
2,2,4-trimethylpentane[*]
Formaldehyde[*]
Ethylbenzene[*]
o-xylene[*]
Methylbromide[*]
2-butanone[*]
1,3-dichloropropene[*]
Methyl isobutyl ketone
Acetaldehyde[*]
Manganese[*]
Antimony[*]
Lead[*]
Nickel[*]
Arsenic[*]
Cadmium[*]
Chromium[*]
Mercury[*]
Phosphorous
Others

[a] Informally, Mexico follows a similar listing for airborne toxics as adopted for HAPs in the US. Mexican authorities (Gobierno del Distrto Federal 2007) completed in 2006 their first urban air toxics inventory for the metropolitan zone of Mexico City (The Valley of Mexico-ZMVM). The species of concern are listed in Table 6-1c. The inventory provides a first insight into the nature and speciation of selected air toxics in the Mexico City region for both stationary and mobile sources. The total emissions are estimated to be approximately 175,000 t per year

[*] Denotes species included in US EPA HAP list

Chapter 1
Executive Summary

William T. Pennell

In 2007, NARSTO was charged with assessing the technical challenges of transitioning from a pollutant-by-pollutant approach to air quality management to the risk-based, multipollutant approach suggested by the U.S. National Research Council in 2004 (NRC 2004). NARSTO's assessment examines current scientific capabilities for achieving a risk-based multipollutant approach to air quality management that also includes a system for assessing the effectiveness of individual air quality management actions; i.e., accountability. The charge to the assessment team was not to provide a roadmap for implementing multipollutant air quality management and accountability but to assess the state of the knowledge and tools for achieving such a management approach and to recommend areas where capabilities and knowledge could be improved. In developing the assessment's conclusions and recommendations, the assessment team considered risk assessment methodologies, atmospheric processes and modeling, measurements and monitoring systems, emissions, climate and other future global-scale changes, and current air quality management initiatives. Although the NRC (2004) recommendations were directed toward the air quality management system in the United States, they are also of great interest to Canada and Mexico as both countries continue to improve the efficiency and effectiveness of their air quality management programs. This assessment does take a North American perspective; however, the authors believe the findings and recommendations should be of interest to other countries as well.

The current frameworks for managing air quality in Canada, the United States, and Mexico (see text box) are well established and generally have been successful in reducing air pollution, especially in urban areas. However, we believe that air quality management can be made more efficient and effective by addressing sources, atmospheric concentrations, exposure, and effects holistically.

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Air Quality Management in North America

Air quality regulations are designed to protect human health, ecosystems, and air-quality related values, such as visibility. The priority in Canada, the United States, and Mexico has been to reduce ambient concentrations of air pollutants that affect large urban portions of North America and pose adverse health consequences for the general population. Following U.S. practice, we refer to these pollutants as criteria pollutants. Traditionally in all three countries, ambient air concentration standards or objectives are set for each criteria pollutant at values that protect the public from adverse health consequences within some adequate margin of safety. The management approach in each country is to specify emission controls, or emission capping or reduction programs, to reduce ambient concentrations while treating each criteria pollutant (or its equivalent) individually. In practice, however, air quality managers do consider physical and chemical interactions among pollutants and how actions taken to address one pollutant might affect others, especially with respect to secondary pollutants like ozone or fine particles.

In addition to the criteria pollutants, certain air pollutants pose concerns because of their specific toxicity or cancer-causing potential. Emissions of these pollutants, called air toxics or hazardous air pollutants, are generally much smaller than those of criteria pollutants, although some sources emit both hazardous and criteria air pollutants. Hazardous air pollutants are regulated (primarily in Canada and the United States) through emission standards or other actions designed to limit individual (as opposed to population) risk. Hazardous air pollutants can also be formed via chemical reactions in polluted atmospheres, and atmospheric processes affect them in ways similar to criteria pollutants. Hazardous air pollutants formed through chemical reactions in the atmosphere have not been a specific focus of air quality standards or management actions.

In addition, air quality management actions can be integrated with measures taken to mitigate anthropogenic contributions to climate change. This latter point is important because common air pollutants (e.g., carbon monoxide, nitrogen oxides, ozone, and particulate matter) can affect the climate; climate change can affect air quality-related emissions and conditions conducive to the formation of air pollution; and policies adopted to reduce emissions important to one problem (air pollution or climate change) can have consequences for the other.

1.1 Features of Risk- and Results-Based Multipollutant Air Quality Management

A risk- and results-based multipollutant air quality management approach has the following features:

- *Administrative Coordination:* All air pollutants and climate-forcing agents are considered together. Reviews of air quality standards are coordinated and placed on compatible schedules. Plans for achieving the standards or desired emission reductions (and analyses of the consequences of these reductions) are coordinated and placed on a common timeline.
- *Risk-Based Decision Making:* When multiple pollutants are controlled simultaneously, the likelihood is even greater that there will be complex changes in exposures to humans and inputs to ecosystems. Thus, air quality management actions should address the greatest integrated risks to human health, ecosystems, and public welfare rather than achieving each ambient standard simultaneously.
- *Accountability:* Results-based multipollutant air quality management includes a formal procedure for assessing progress in implementing air quality management actions, evaluating the effectiveness of these actions in achieving the desired goals, and demonstrating the value of these actions in protecting human health and ecosystems. Accountability goes beyond simple compliance monitoring. In its fullest expression, its goal is to determine whether the action in question is achieving predicted reductions in risks to human and ecosystem health, and if not, why.

1.2 Risk Assessment and Accountability in a Multipollutant Air Quality Management Environment

Figure 1.1 depicts how risk assessment and accountability are linked in a risk- and results-based air quality management environment. Risk assessment is already a part of the air quality management framework in North America. Estimates of risk are employed, to some degree, in setting standards and in designing air quality management actions for meeting these standards. Estimates of risk are derived from the sequence of identifying health and ecological hazards, defining human and ecosystem exposures, and merging hazard and exposure into qualitative and quantitative characterizations of risk.

Risk characterization (the blue-bordered boxes in Fig. 1.1) is an assessment of whether a particular substance has the potential to cause harm to public health or to the environment, and it is a key step in the risk assessment process. Exposure assessment is critical to risk characterization; exposure assessment uses emission inventories, measurements, and emission-based air quality modeling to estimate ambient concentrations of hazardous substances. These concentrations are then used as a surrogate for personal exposure, or they are coupled with human time and activity modeling and other information needed to establish micro-environmental concentrations to estimate personal exposure. Exposure estimates and available concentration-response or exposure-response information then support an estimate of the health or environmental impacts of the substance in question.

If a substance is identified as posing a significant risk, it may be subject to an air quality management action, as indicated by the steps bordered in red in Fig. 1.1.

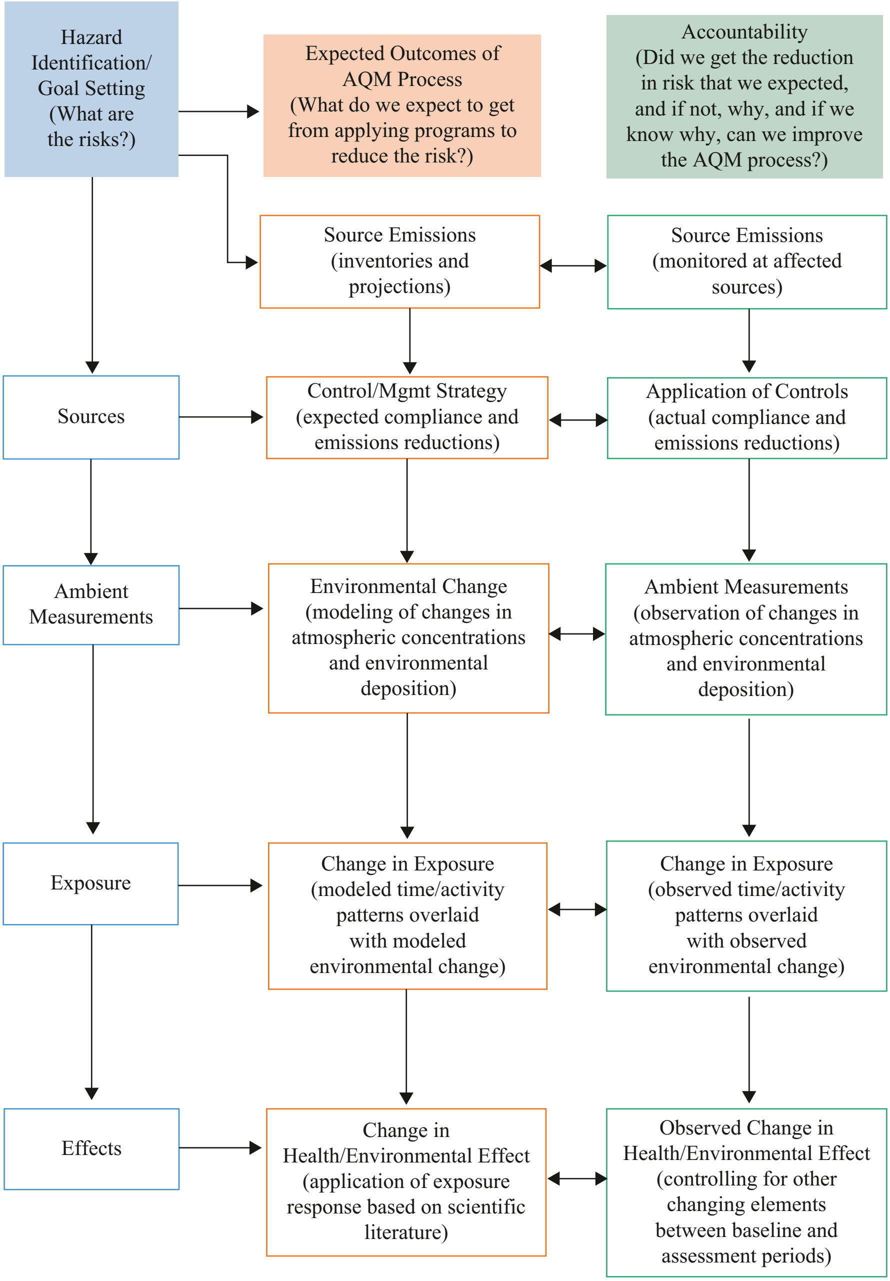

Fig. 1.1 The roles of risk analysis and performance evaluation (accountability) in air quality management practice

As depicted in the figure, development of an air quality management action includes prospective analysis for determining the reductions in emissions, ambient concentrations, and exposure that may be needed to reduce the risk to a desired level of protection. This analysis is based on empirical concentration-response or exposure-response evidence that provides guidance on the ambient concentrations or other indicators of exposure that will achieve the desired level of risk reduction. In the case of ecosystem protection (e.g., protecting forests, agricultural resources, watersheds, and biota from adverse effects of pollutant exposure) or in the assessment of risks associated with hazardous air pollutants, the risk assessment process includes similar exposure and effects assessment in preparing appropriate management decisions.

Risk assessment is used in single pollutant air quality management, but it has not typically been used to assess *relative* risk across pollutants. Under a fully realized multipollutant air quality management regime, however, assessment of relative risk becomes essential. Here, decisions need to be made with regard to multiple pollutants involving multiple sources based on the proposed air quality actions that result in the greatest, or most effective, reduction in the risk of adverse health or ecosystem effects. Decisions may hinge, therefore, on our ability to determine relative risks due to exposure to multiple pollutants, assessed separately, or the risks of exposure to mixtures of pollutants. Decisions may also vary between and within airsheds. For example, mobile sources may present the greatest risk in one airshed, while industrial sources may pose the greatest risk in another. Within an airshed, mobile sources could pose the greatest risk for those living in close proximity to major roadways, while in another part of the airshed other sources (local or regional) could be more significant.

As with risk analysis, performance assessment (or accountability) can be applied in both single pollutant and multipollutant air quality management paradigms. Unlike risk analysis, however, a formal, complete accountability process has not been an integral part of past air quality management programs. As is depicted in the green-bordered boxes in Fig. 1.1, an accountability analysis is implemented through a series of steps sometimes called the accountability chain. These steps determine whether:

1. The management action was implemented as designed and the expected emission reductions have taken place.
2. The actual or estimated emission changes resulted in the expected changes in ambient concentrations or deposition.
3. The changes in ambient concentrations or deposition have resulted in reductions in exposure of humans or ecosystems to the pollutants in question.
4. These reductions have led to improved public health or reduced damage to sensitive ecosystems.

In addition to measuring the effectiveness of air quality management actions, accountability can also be part of a process of continuous improvement. Each step down the accountability chain provides information that can be used to improve the effectiveness or, perhaps, lower the cost of the original air quality management action. These attributes of accountability—measuring effectiveness and providing corrective feedback—are illustrated by the double-arrow lines in Fig. 1.1.

A major challenge of accountability is that each step down the accountability chain—from emission reductions to health or ecosystem effects—represents an increase in the probative value of the information; however, with each step down the chain it becomes increasingly difficult to establish a clear cause and effect relationship. Emission changes, for example, may result from changes in economic conditions or from the adoption of new technology for reasons unrelated to air quality management. Also, verifying emission changes is not a simple matter for sources not equipped with continuous emission monitoring systems. Likewise, the principal health effects attributed to air pollution (e.g., respiratory stress and heart disease) are also driven by other confounding factors, some of which have much greater impact on one's susceptibility to developing these diseases (e.g., tobacco smoking or changes in health care practices) than ambient air pollution.

The problem of establishing the cause, effect, and benefits of changes in air quality becomes particularly difficult for air quality management actions implemented over a number of years. The longer it takes to implement an air quality management action, the greater the possibility that any observed health or ecosystem outcomes will be affected by confounding factors or that additional actions will have taken place during the same timeframe that complicate the ability to attribute cause and effect.

True accountability goes well beyond the compliance monitoring usually conducted to assess attainment of ambient air quality standards. A complete accountability program that links sources to effects requires advance planning to ensure that the necessary methods and data will be available to provide the level of proof desired. If accountability becomes a formal part of air quality management, planning for accountability demonstrations should be part of any new rule making. The information needed for an accountability demonstration should be tied directly to the risk assessment indicators and process modeling used in the development of the air quality management action in question. One cannot assume that the necessary information will be available post hoc.

1.3 Transitioning to Risk- and Results-Based Multipollutant Air Quality Management

To facilitate thinking about the issues and to organize presentation of the results, the assessment team postulated a four-level transition from pollutant-by-pollutant management to risk-based, accountable, multipollutant air quality management. Accountability can be implemented at each of these levels. At *Levels 1* and *2*, the emphasis is on determining whether the management actions under consideration have achieved the expected reductions in emissions and ambient concentrations or in atmospheric deposition. At *Levels 3* and *4*, accountability extends to determining whether expected reductions in exposure and, ultimately, human health or ecosystem effects are being achieved.

Level 1. A strict single pollutant perspective with the focus on attainment of individual ambient standards.

In current regulatory administrative practice, air quality management actions are developed to meet single pollutant standards without formal consideration of coincident or cumulative benefits or tradeoffs regarding other pollutants. The current underlying information and many of the assessment tools, particularly air quality models, are capable of addressing multiple pollutants; however, these capabilities are only used to assess efficient pathways to attaining a specific ambient standard or objective in a designated area and timeframe.

At *Level 1*, the focus is on attaining the individual standards, and the schedules for developing plans for attaining these standards are not necessarily coordinated. Nevertheless, improvements in emission information, characterization of relevant atmospheric processes, and ambient monitoring are always needed for improving the effectiveness of individual air quality management plans and for demonstrating attainment of the standards. With respect to accountability, consistent emission information should be maintained over a period of years to allow retrospective assessment of trends, and consistent methods for projecting future emissions are needed to project future ambient concentrations and deposition. At *Level 1*, risk assessment is not part of the accountability analysis. Ambient concentration or deposition results from air quality modeling or monitoring networks are handed over to the exposure and effects communities for determining whether or not attainment of the standards is achieving the desired level of human health or ecosystem protection.

Level 2. Attainment of standards for individual pollutants, but with increasing attention to co-benefits attainable through coordinated emission reductions.

At *Level 2*, the focus remains on attaining individual standards, but in a way that considers and optimizes the co-benefits of emission reductions in attaining standards for other pollutants. For example, current air quality models treat a wide range of chemical and physical processes that affect regulated air pollutants such as ozone (and other photochemical oxidants), particulate matter, and certain hazardous air pollutants. Development of air quality management plans for addressing these pollutants and looking for synergistic benefits in reducing emissions from common source-types is quite feasible. In fact, this approach has been explored in the South Coast Air Quality Management District in California and the state of Georgia. Such an approach, for example, might consider the coincident benefits of reducing ambient concentrations of hazardous air pollutants and particulate matter in a strategy designed for ozone reduction, or the coincident ozone reduction benefits of a strategy focused on particulate matter. Such approaches are being considered within the U.S. EPA, and one experimental study has been recently completed in Detroit, Michigan. More detail on these activities, as well as documentation of and support for the conclusions and recommendations provided in this summary, are found in the relevant chapters of this book.

Level 3. Management decisions based on achieving greatest risk reduction based on single pollutant exposure-dose-response relationships.

In contrast to *Levels 1* and *2*, *Level 3* envisions the development and evaluation of emission reduction strategies that simultaneously meet multiple air quality (and deposition) targets or standards without constraining the analysis to meet a single priority target. This approach implies the concept of trade-offs and prioritization of actions based on which actions address the most significant risks or achieve the greatest net reductions in risk, assuming that all risks are additive. This approach requires that target goals (e.g., ambient standards, deposition targets, or benchmark concentrations associated with an agreed-upon risk threshold) be associated with each individual pollutant under consideration, and it requires a formal procedure for conducting risk assessment (including methods for comparative assessment on health risks and ecosystem benefits). Such a formal optimization analysis requires a complex integrated assessment model and appropriately accurate information on the risks associated with the individual single pollutant targets. Such models have been developed, and they could be applied when the appropriate data and evaluation measures are available.

Level 4. Management decisions based on achieving greatest risk reduction based on multipollutant exposure-dose-response models.

Level 4 considers a variety of emission reduction strategies evaluated on the basis of net risk reduction or maximum benefit, taking into account the synergistic effects of exposure to multiple pollutants when such effects exist. This level of multipollutant air quality management assumes the availability of exposure-response functions (and, ideally, evaluation measures) for groups or mixtures of pollutants. By incorporating overall risk reduction, *Level 4* allows for the development and evaluation of comprehensive strategies for the protection of human health and ecosystems. *Level 4* recognizes that the effects of exposure to multiple pollutants range from increases to decreases in the adverse impacts that might be expected by summing individual exposure-response relationships.

1.4 Assessment Conclusions and Recommendations

The purpose of this assessment is to evaluate the technical challenges of implementing a risk-based, results-oriented multipollutant approach to air quality management. The assessment team was asked to evaluate the state of the science now and over the next 5–10 years, and to recommend actions that might be taken to improve it. The assessment follows two threads of thought (1) risk-based multipollutant air quality management and (2) accountability, which is the measurement of results. Multipollutant air quality management could be implemented without accountability, and accountability could be applied to the current, largely single pollutant, air quality management approach. Consequently, we group the conclusions and recommendations of this assessment by those that apply largely to multipollutant air quality management and those that pertain to accountability. In a few cases there may be some overlap.

1.4.1 Multipollutant Air Quality Management

While current air quality regulations generally address single pollutants, most current control strategies address multipollutant interactions; for example, they take into account how actions taken to address one air pollutant (e.g., ozone) may affect another (e.g., $PM_{2.5}$). Contemporary air quality models can account for ambient chemical interactions among regulated pollutants and estimate how changes in multiple emission sources might affect ambient concentrations for several pollutants simultaneously. *Thus, the basic technical capabilities for developing coordinated emission reduction approaches to controlling air pollution and implementing multipollutant air quality management at Levels 1 and 2 currently exist—as long as sufficiently complete and accurate information on emissions is available and the criterion for success is attaining ambient air quality goals or deposition and emission reduction targets.*

However, the risk-based multipollutant air quality management approach (*Levels 3* or *4*) requires that we have the ability to develop multipollutant management strategies that address "the most significant exposures [and] risks…" and "accomplish comprehensive reductions [in these risks or exposures] in the most cost-effective manner for all priority pollutants" (NRC 2004). In principle, risk analysis frameworks already exist that are suited for analyzing alternative multipollutant management actions. Emission modeling and air quality modeling elements of these frameworks are already multipollutant in character. The principal missing resources are (a) comparable exposure-response information that enables determination of the relative risks of exposure to single and multiple pollutants and (b) improved methods for comparative evaluation of health and ecosystem benefits.

The first step (*Level 3*) in an evolution to a full risk-based multipollutant approach to air quality management is to assess risk on the basis of exposure to multiple individual pollutants. Alternative management strategies can be compared by determining which are most effective in reducing exposure to the pollutant that represented the highest population (or individual) risk or the greatest net benefit assuming all risks were additive. *However, while we have information on the risks of exposure to individual criteria pollutants and some air toxics, this information contains significant uncertainties. These uncertainties include not only those associated with determining exposure, dose, and effect, but also, in some cases, uncertainties in whether the pollutant in question is the actual cause of an adverse effect or a surrogate for that effect. Although our knowledge may be sufficient for setting standards, these uncertainties are currently too great to allow a complete ranking of the severity of risk of exposure to individual pollutants. Partial rankings are feasible where there are large differences in the levels of exposure or toxicity and the agent causing the adverse effect is known unequivocally.*

The next step in implementing a risk-based multipollutant approach to air quality management (*Level 4*) requires an assessment of the effects of simultaneous exposure to multiple air pollutants. *Little is known about the human health and ecosystem effects of exposure to mixtures of pollutants other than to consider co-pollutants* *as confounders of the effects of the principal pollutant under consideration. Therefore, it is unlikely that this level of multipollutant air quality management could be implemented within the next five to ten years*. Investigators have had little incentive to sort out the causal components of pollutant mixtures except for studies of the effects of acidification on freshwater ecosystems. Epidemiology has had little power to address potential synergisms, but there is evidence from experimental exposures of humans and animals in laboratory environments that some combinations of pollutants cause greater, and in some cases fewer, than additive effects. Thus, current knowledge indicates that the potential for synergies (or antagonisms) cannot be ignored. With respect to ecosystems, interactions between metals and acidity, as well as combinations of certain persistent organic pollutants, could have adverse synergistic effects in aquatic systems. *If a comprehensive multipollutant approach to air quality management is to be pursued, more attention will need to be given to the consequences and risks of multipollutant exposure. With respect to air toxics and human health, toxicological information could be used for relative risk assessment on the basis of potency* (*or reactivity*) *and exposure. However, little of this kind of relative risk assessment has been performed.*

An alternative to moving beyond an approach to air quality management that focuses on attainment of individual ambient air quality standards is to focus on reducing the most significant exposures—those presenting the greatest risks, based on current knowledge, for the greatest number of people. *With improved capabilities for characterizing exposure, air quality management actions could be prioritized according to which might be most effective in reducing exposure of broad population categories to the pollutants or combinations of pollutants presenting the greatest risks as we currently understand them* (*and setting the stage for future accountability analysis and mid-course correction of management strategies*).

A further advance in multipollutant air quality management might be achieved through grouping approaches in which pollutants such as air toxics are treated collectively on the basis of reactivity, where such characteristics have been linked to a key biological mechanism of harm. Other approaches to dealing with the health effects of pollutant mixtures could also become available in the future. For example, the emerging field of computational toxicology (which involves the integrated application of genomics, proteomics, and advanced computational models) may offer fresh approaches to examining the toxicology of mixtures and assessing their effects.

Lastly, future air quality management in North America could be complicated by three global-scale multipollutant influences:

- Hemispheric transport of long-lived pollutants and pollutant precursors due to increased global emissions, which could affect local and regional air quality management by increasing ambient background concentrations.
- Changes in precursor emissions, within North America as well as globally, that result from actions taken to mitigate anthropogenic climate change.
- Changes in atmospheric chemistry, biogenic emissions, and meteorological conditions brought about by climate change.

In principle, we have the observational and modeling tools needed to assess the effects of hemispheric transport on air quality. Also, modeling simulations indicate that climate change will not radically change our general approach to mitigating poor air quality, although climate change could affect the frequency and intensity of poor air quality episodes and increase the challenge of meeting air quality management goals. Perhaps the most dramatic effect of climate change on air quality, at least in the medium to longer term, could be the changes in emissions brought about by climate change and actions that might be taken to reduce it. Addressing climate change through the reduction of climate-forcing emissions will require major changes in fuel uses and in energy-production and end-use technologies. These changes, in turn, will have significant effects on air quality related emissions. Because a number of air pollutants and pollutant precursors have the power to affect climate change, it is important to take these changes into account and to pursue climate and air quality policies that generate synergistic benefits for both problems.

Should the decision be made to adopt risk-based multipollutant air quality management, we recommend the following high-priority actions for developing the knowledge needed to enable this transition:

Multipollutant Air Quality Management Recommendation 1: *Improve the ability to assess pollutant exposure.* Achieving the objective of risk-based multipollutant air quality management will require improved characterization of human exposure to a wider range of air pollutants within a broader spectrum of microenvironments and exposure scenarios. This requirement is the most important advance needed to improve our understanding of pollutant-health relationships not only for air quality management but also for sharpening our understanding of the effects of air pollution on human health and ecosystems. Achieving this goal will require new or enhanced measurement methods and monitoring strategies (see Multipollutant Air Quality Management Recommendation 4) as well as modeling tools that support improved exposure assessment for both human-health and ecosystem-effects studies and a commitment to verify the exposure estimates provided by these measurement systems and models. These systems, strategies, and models will need to provide information with the temporal and spatial resolution needed to represent the ambient concentration gradients associated with the pollution sources of concern. They will need to account for geographically specific outdoor conditions, infiltration into buildings and vehicles, and human activity patterns. These data must go beyond the information needed to document concentration distributions and trends of regulated pollutants for conventional compliance purposes and include other pollutant species that may pose health or environmental risks.

Multipollutant Air Quality Management Recommendation 2: *Expand the focus of health and ecosystem effects research to include the effects of exposure to multiple pollutants and place increased emphasis on this problem.* Encourage the formation of broad multidisciplinary research teams (including atmospheric, exposure, health and ecological scientists) and direct these teams to focus on the following strategic questions: (1) What are the health and ecological damage burdens of air pollution in relationship to other environmental stressors? (2) Which pollutants and combinations of pollutants actually cause which effects, which pollutants dominate these effects, how do they interact, and how can we reduce uncertainty about the effects of exposure to single pollutants? (3) Is it feasible to group pollutants according to chemical structure or type, or some other feature, in order to expedite research on the effects of exposure to multiple pollutants? (4) Can we construct objective metrics for prioritizing health versus ecosystem effects? The emphasis in addressing these questions should be on improving our understanding of the risks of exposure to pollutant mixtures and of the relative risks of exposure to individual pollutants.

Multipollutant Air Quality Management Recommendation 3: *Improve emission information and emission control technologies.* Improvements in emission information should include (a) implementing the recommendations of the NARSTO Emission Inventory Assessment (NARSTO 2005), (b) improving communication between the health effects and emissions information development communities to ensure that emissions inventories include, to the extent feasible, all substances thought to pose risks to human health and ecosystems, (c) expanding the range of substances and sources that can be measured directly, and (d) encouraging the development of multipollutant emission control technologies that could reduce the cost and improve the effectiveness of emission reduction programs.

Multipollutant Air Quality Management Recommendation 4: *Modify the designs of air quality measurement programs to enhance support for multipollutant air quality management.* Present air monitoring programs in North America are designed primarily to demonstrate compliance with ambient air quality standards. Nevertheless, they do support some multipollutant surveillance. Thus within the current system, there are opportunities to shift resources to improve support for multipollutant air quality management. Examples include: (a) expanding measurement of oxidants, speciated volatile organic compounds, and particulate organic compounds, (b) expanding the measurement capabilities of current monitoring systems by using advanced instrumentation already proven to be reliable, (c) coordinating current measurement objectives with those needed to support epidemiological studies, including provision for at least occasional intermittent sampling in areas of strong concentration gradients (e.g. roadway zones), and (d) conducting special campaigns to measure exposure-related parameters and non-regulated species including oxidants, a wider range of reactive nitrogen species, and ammonia. In Canada, there is a need to add one or two multipollutant sites in the northern portion of the country in order to improve coverage in remote regions. In Mexico, there is a need to continue expand permanent measurements in cities and population centers other than the Valley of Mexico, and add at least one regionally representative multipollutant site in rural, central, or northern Mexico.

Multipollutant Air Quality Management Recommendation 5: *Undertake one or more pilot studies of the feasibility of implementing a risk-based, results-oriented multipollutant approach to air quality management.* The current technical capabilities for developing coordinated emission reduction approaches to controlling air pollution and implementing multipollutant air quality management at *Levels 1* and

2 should be expanded. As a first step in a transition to a multipollutant approach, additional pilot studies, such as the one recently completed in Detroit, Michigan are needed to assess the feasibility and advantages of coordinating management of criteria pollutants and air toxics. They are also needed to examine the extent to which we can demonstrate accountability and use it as a management tool. Although some initial steps have been taken in the United States to explore multipollutant air quality management approaches (principally at *Level 2*), these efforts have not encompassed the scope proposed here, which implies development of approaches to implementing *Level 3* and ultimately *Level 4* multipollutant air quality management plans.

Multipollutant Air Quality Management Recommendation 6: *Analyze the potential effects of technological change, especially those changes related to climate change, on future air quality and its effects on human health and ecosystems.* The objective of this research should be to characterize the effect of new fuels or changes in primary production or end-use energy technologies, adopted to reduce greenhouse gas emissions and climate-affecting particles, on air quality as well as the effect of future air quality management actions on the production of climate-forcing agents. The scope of this research should also include investigations of how a changing climate might affect natural emissions of greenhouse gases, particles, and greenhouse gas and particulate precursors.

1.4.2 Accountability

Accountability is a formal procedure for determining whether a given air quality management action or combination of actions have achieved their intended benefits. In addition to measuring the effectiveness of air quality management actions, accountability can also be part of a process of continuous improvement. Each step down the accountability chain provides information that can be used to improve the effectiveness or, perhaps, lower the cost of achieving air quality management goals; however, with each step it becomes increasingly difficult to establish definitive outcomes and a clear cause and effect relationship.

Considerable evidence shows that past air quality management actions have resulted in improved air quality (i.e., reduced ambient concentrations) for criteria pollutants. Emerging evidence also shows that actions taken to reduce ambient concentrations of ozone and particulate matter have led to reductions in adverse health effects associated with exposure to ambient concentrations of these pollutants. Reductions in emissions of acid-forming substances, especially sulfur dioxide, have led to reductions in acidic deposition and improvements in water quality in many sensitive surface waters. *However, no formal, complete retrospective analysis, through the accountability chain, has been performed on a specific air quality management action to determine whether the expected results of the action was achieved in practice. Consequently, we strongly recommend a formal, quantitative demonstration that mandated emission reductions have been achieved along with the expected changes in ambient concentrations or deposition.*

Accountability Recommendation 1: *Two or more retroactive test cases should be undertaken to demonstrate the current capability for determining full accountability for past major air quality programs or rules.* These test cases should bring together the best available information in a formal assessment down the accountability chain and serve as a starting place for future accountability improvement.

As the first step in implementing this recommendation, we strongly recommend that the ability to achieve at least step 2 of the accountability chain (verification that actual or estimated emission changes resulted in the expected changes in ambient concentrations or deposition) be explored before accountability is mandated as a component of future air quality management decisions. *The difficulty in determining whether discrepancies between predicted and observed changes in ambient air quality or deposition are due to errors in emission information, deficiencies in our understanding of the relevant atmospheric chemistry or atmospheric processes, errors or deficiencies in the representation of important chemical or other atmospheric processes in the air quality models used, the impact of predicted versus actual meteorology, or in the way the models were implemented* (*or all of the above*) *should not be underestimated.*

In Mexico, the principal source of data to establish trends in ambient air quality for criteria pollutants is the Valley of Mexico (Mexico City). To facilitate the establishment of broader accountability in Mexico, we recommend that development of their national monitoring network be pursued as rapidly as practical. Further, there is a need in Mexico for a sustained survey of air toxics in urban areas beyond currently conducted in Mexico City.

Achieving step 4 of the accountability chain (verification that reductions in exposure have led to improved public health or reduced damage to sensitive ecosystems) will not be easy. *Epidemiological and toxicological research indicates that common air pollutants have adverse health effects, but determining the health benefits of gradual reductions in the ambient concentrations of these pollutants due to a specific air quality management action is difficult. Few, if any, health impacts associated statistically with air pollution are caused solely by exposure to air pollution, and the portions attributable to pollution are uncertain. Moreover, demography and other factors that affect exposures leading to health effects can change on the same time scale as improvements in air quality.* The strongest evidence for human health benefits from reductions in air pollution comes from so-called "natural experiments" or "intervention studies" in which large and relatively rapid reductions in emissions leading to improvements in air quality are accompanied by reductions in certain health burdens among the affected population. In contrast to intervention studies, most air pollution control measures take effect gradually, and most estimates of pollution-response relationships take the form of concentration-effect slopes or potency factors (i.e., risk per unit of pollutant concentration). Health gains can result from reduction of exposure, reduction of potency (in the case of multi-component classes such as PM), or both. Misattribution or underestimation of health gains can occur if factors unrelated to pollution, but capable of mitigating or masking the change in health burden, change over the same period that pollutants are reduced in concentration or potency. Thus, demonstrating that specific air quality management actions have resulted in improvements in human health (or ecosystem function) is extremely difficult, and it can take a long time (perhaps 20 years or more) for the signal (e.g., reduced mortality due to air pollution exposure) to emerge from the noise (all other confounding factors). Such demonstrations can probably be done and, as stated above, there is emerging evidence of the population health benefits of reduced exposure to ambient concentrations of lead or fine particles. Demonstrating changes in health effects related to pollution exposure requires carefully designed epidemiological experiments that are executed in concert with the air quality management action and maintained over extended periods of time. It may also be difficult to sort out which air pollutant may be responsible for what effect. People and ecosystems are exposed simultaneously to many air pollutants and exposure to them may be highly correlated. It is difficult to determine the effects of individual pollutants because little is known about the combined effects of exposure to multiple pollutants, which may not be additive. It is also possible that the air pollutant thought responsible for a given effect may only be an indicator of exposure to some other substance that is correlated with it.

Accountability for effects of air pollution exposure from deposition to vulnerable ecosystems has advanced in similar ways to that of human health effects, especially for acidification of aquatic systems. Changes in terrestrial ecosystems with pollution reductions have been difficult to verify not only for acidic deposition, but also for oxidants, trace metals, and persistent organic pollutants. Changes in chemistry of vulnerable surface waters from reduction in sulfur oxide emissions and sulfate deposition have been documented semi-quantitatively in accordance with expectations of emission reductions in eastern North America. However, the recovery of biota has been far slower than the response in water chemistry. Research to date has shown the difficulty in attributing changes in managed or unmanaged terrestrial ecosystems systems to reductions in exposure to contemporary levels of air pollution (including acids, acid gases, oxidants, metals or persistent organic pollutants) for reasons similar to those found for humans. *Additional support for long-term surveillance of representative ecological sites would assist the verification of expected changes in relation to pollution exposure, not only in water and soils chemistry, but also in biological changes involving species survival and diversity.*

Accountability Recommendation 2: *Verify and improve emission estimates from model-estimated source categories.* Characterizing and verifying changes in emissions from sources equipped with continuous emissions measurement systems are relatively simple. However, it is much more difficult for the large number of mobile, complex industrial, small point-sources, and area-sources for which emissions must be estimated by means of emission models. *Uncertainties in, and in some cases the lack of information on, emissions responsible for adverse health and ecosystem outcomes remains a fundamental barrier to implementation of formal accountability procedures.*

Model verification and improvements must include better speciation information that encompasses, to the extent possible, all substances known or suspected to adversely affect human health or ecosystems. Specific examples include:

- Improving on-road and non-road mobile source emission models by measuring exhaust and evaporative emissions from statistically representative samples of in-use vehicles or equipment for a representative range of environmental conditions and operating modes. Improved characterization of volatile organic compounds, semivolatile organic compounds, and carbon particulate emissions are of particular interest. The use of micro-sensors for continuously measuring oxides of nitrogen, carbon monoxide, volatile organic compound emissions coordinated with measurements of carbon dioxide or fuel consumption would be a valuable innovation.
- Improving estimates of ammonia emissions from agricultural sources and verifying these models for the range of climatic conditions, agricultural economies, and agricultural practices across North America.
- Instituting focused research and development programs for characterizing emissions and improving emission estimates for important source categories (including climate-relevant emissions such as those from transportation and industrial sources as well as emissions of air toxics and nitrogen species), which will vary by country and by region.
- Increasing information exchange between the health effects and emissions characterization communities to ensure that emissions thought to pose the greatest health-risk potential are measured or modeled accurately over a range of space and time scales. Such emissions information may include substances not included in traditional emissions inventories.
- Maintaining continuity and comparability in a time-continuous record of emissions inventories to enable retrospective analyses of past air quality management actions. Particular emphasis needs to be placed on documenting changes in emissions developed from models that are frequently updated to incorporate methodology improvements. Not having this information hampers the ability to compare results over time.

An important priority for Mexico should be to undertake an assessment of the adequacy of current emission inventories for supporting an accountability assessment of the effectiveness of current air quality management actions in reducing concentrations of ambient pollutants. This demonstration could focus initially on the effects of reducing sulfur concentrations in transportation-sector fuels.

Consideration should also be given to increasing, where practical, the number of large point sources in North America equipped with continuos emission monitoring systems. Furthermore, we recommend that a significant level of funding be provided, through mechanisms such as the U.S. Small Business Innovation Research program, for the development of small, potentially low-cost, emission measurement systems that would increase the number of source categories that could be measured directly either on an operational basis or for improving the accuracy of emission models.

Accountability Recommendation 3: *Identify reliable biomarkers of exposure for a larger number of air pollutants.* Air quality goals for criteria air pollutants are generally expressed in terms of ambient concentrations, and it is assumed that attainment of these goals will be reasonably protective of human health. However, knowing broad-scale average ambient concentrations is often insufficient for determining human exposure and, eventually, dose. First, for many pollutants current ambient monitoring and air quality modeling do not supply information on the spatial and temporal scales relevant to actual individual exposures. Ambient concentrations of pollutants associated with many sources of concern, such as high traffic-density roadways or toxic air pollutant "hot spots," may vary sharply with distance from the source, with season, or with time of day. Second, estimating exposure to pollutants of ambient origin requires knowledge of how and for how long affected individuals move through this concentration space, what they are doing while they are there, the infiltration of ambient pollutants into indoor environments occupied by affected individuals, as well as other factors.

Given the difficulty of estimating exposure from measurements and modeling, identification and validation of additional biomarkers of exposure to a wider range of air pollutants could greatly facilitate accountability analyses and should be a priority research objective. Except for lead and carbon monoxide, exposure to criteria air pollutants is generally not associated with specific, identifiable effects or biomarkers. The situation with respect to hazardous air pollutants, however, appears to be more hopeful. There has been considerable progress in identifying biomarkers of exposure to hazardous air pollutants, particularly for carcinogens. These markers are useful for characterizing total exposure to many compounds that are found in the air, noting that most of these species can also enter the body via other routes. Despite these challenges, the availability and utility of biomarkers of exposure to air pollutants is improving, and their use as indicators of exposure are expected to receive increased attention in multipollutant studies.

Accountability Recommendation 4: *Rethink current monitoring network design and sampling strategies and focus their mission on providing the information needed for improved exposure assessment. Continue the development of improved exposure assessment models and methodologies for exploiting exposure-focused observations.* For pollutants having no practical biomarkers, exposure must be estimated using a combination of measurements and modeling tools. Measurements and modeling tools may also be needed to supplement the information deduced from biomarkers. If the ambient concentrations of the pollutant or pollutants in question are relatively homogeneous in space and time, assessing the impact of air quality actions on exposure is relatively straightforward. Estimating exposure for pollutants presenting significant spatial and temporal variability, however, will require improvements in exposure modeling procedures and monitoring network design. Given sufficient investments, we believe that significant improvements in exposure information are possible within the near future (i.e., five to ten years).

The spatial and temporal detail required for exposure assessment cannot be generated by monitoring alone. Exposure characterization will require a more nuanced approach that combines long-term monitoring measurements with modeling and intensive diagnostic measurement campaigns that provide practical estimates of the appropriate ambient concentrations. These estimates, combined with improved exposure models, can then be used to provide estimates of individual exposures (as needed for some air toxics), or population exposures (as needed for some criteria air pollutants). Development of approaches for providing the kinds of detailed ambient concentration fields needed for exposure assessment will require implementation of a number of field studies in several venues across North America in order to test and evaluate the new methods, monitoring network designs, sampling strategies, and data analysis procedures that would be required to take accountability to this level of detail.

Accountability Recommendation 5: *If accountability is adopted as a tool for evaluating and adjusting air quality management actions, it must become an integral part of the air quality planning and rulemaking process.* A technically credible accountability program would demonstrate the linkages in the accountability chain from emissions to exposure; it would demonstrate that the accountability metrics can be determined to some reasonable level of statistical uncertainty; and it would need to be adequately funded.

1.5 Final Remarks

A multipollutant approach to air quality management is currently feasible through *Level 2* (attainment of standards for individual pollutants, but with increasing attention to co-benefits attainable through coordinated emission reductions); coordination of air quality management actions at this level could have considerable benefit. Given sufficiently accurate emission information, accountability through Step 2 (verification that the air quality management action in question has achieved the expected reductions in ambient concentrations or deposition) is feasible and could provide valuable information for assessing or improving air quality management actions. However, it is recommended that this conclusion be tested before this level of accountability is made a formal part of the air quality management system.

Implementing higher levels of multipollutant air quality management and accountability is problematic in the near term, because key exposure and human or ecological health information is not available. The exception might be in considering a multipollutant approach that focuses on exposure. Given improved exposure characterization, air quality management actions could be prioritized according to which might be most effective in reducing exposure for broad population categories to the pollutants or combinations of pollutants presenting the greatest risks as we currently understand them.

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Chapter 2
Introduction

George M. Hidy, Jeffrey R. Brook, Kenneth L. Demerjian, Luisa T. Molina and Richard D. Scheffe

Forty years of efforts to improve air quality in North America, guided by the Clean Air Act in the United States and analogous legislation in Canada and Mexico, have produced a sound scientific understanding of air pollution phenomena and have enabled decision makers to develop effective science-based policies and programs to reduce air pollution. However, air pollution management throughout North America historically has focused on individual pollutants, with little emphasis on the potential interactions of the complex mixture of trace gases and particles generated by anthropogenic and natural activity.

In 2004, the U.S. National Research Council conducted a major review of air quality management in the United States (NRC 2004). The NRC recommended a multipollutant approach, including risk-based decision-making and performance-based measures of progress (commonly known as "accountability"), to improve the efficiency and effectiveness of air quality management. To address the NRC's recommendation in a North American context, NARSTO has assessed risk assessment, health and ecosystem effects, atmospheric chemistry, emission inventories, air quality models, emission measurements, and ambient monitoring systems as well the impact of global-scale influences, including climate change, on air quality management.

The assessment includes definitions of terms (p. xxi et seq.) and begins with a summary of present air quality management practices in Canada, the United States, and Mexico, and a proposal for transition to a risk- and results-based multipollutant approach. The assessment concludes with case studies that illustrate existing tools for evaluating environmental risks and provide examples of methods for tracing changes in emissions to environmental exposure and health improvements. Conclusions and recommendations regarding the future of multipollutant air quality management complete the assessment. Appendices that capture additional technical information are found on the NARSTO web site (www.narsto.org). In addition, the List of Terms at the beginning of this assessment defines terms used throughout the document.

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Decision Making Framework for Air Quality Management (Chap. 3): The assessment begins with a brief review of the current single-pollutant oriented decision making framework in North America. While it was not NARSTO's charge to develop a multipollutant and accountable approach, we do propose steps for transitioning to a full multipollutant management approach as a framework for evaluating information needs.

Risk-Based Assessment and Management Framework (Chap. 4): Risk analysis begins with risk characterization, e.g., human health effects and ecosystem effects in response to an exposure measure. Prospective risk analysis establishes the risk reductions expected to occur as a result of an air quality management action. Accountability, or retrospective risk analysis, establishes the effectiveness of the air quality management action, and allows for changes to the air quality management actions to improve effectiveness or efficiency.

Health Assessment Aspects of Risk- and Results-Based Multipollutant Air Quality Management and Ecosystems (Chaps. 5 and 6): Estimating exposure is a key step in risk assessment. Exposure must be estimated either by air quality and exposure modeling or by direct measurement. The states of knowledge of exposure estimation and consequent human health response are described in Chap. 5. Ecosystem response to pollutant exposure is discussed in Chap. 6, with emphasis on acid deposition, ozone stress and the role of persistent organic pollutants. Also included is the response to certain metal interactions with acid deposition, including mercury.

Atmospheric Science of Air Pollution Phenomena—Current Directions Toward Exposure Characterization (Chap. 7): Knowledge of the multipollutant aspects of atmospheric chemistry is fundamental to air quality management. The principles of chemical equilibria and reactions at the interface between the atmosphere and biological systems are an essential component for addressing air quality and the risks of pollutant exposure.

Source Emissions in Multipollutant Air Quality Management (Chap. 8): An important element in risk analysis and accountability is the projection and verification of air quality or exposure to ambient pollutant conditions. Projections require the application of models, which in turn involve emission estimates. Species identification and quantification in emission estimates are essential components of multipollutant air quality management. Also in this chapter are notes about technological changes and implication for future air quality management strategies.

Atmospheric Modeling (Chap. 9): Air quality models serve as an integrating platform, merging emission data and atmospheric processes to estimate the potential exposure of vulnerable receptors. Air quality models are essential to the analysis of prospective exposure risk, using surrogate (ambient) concentration-response relationships for humans and other biota. Imbedded in air quality models are the relevant meteorological processes of transport and mixing, which influence ambient concentrations and potential exposure. In addition, today's air quality models include sophisticated simulation of chemical reactions in the atmosphere, essential to characterizing multipollutant exposure risk.

Air Quality Measurements (Chap. 10): Because of the complexities of the coupled physicochemical processes in air quality models, measurements are essential for their characterization, even though they are expensive to obtain. Measurements also are an essential part of estimating exposure of humans and ecosystems to pollution. The measurements also are crucial to verifying model performance. Air monitoring and specialized measurement campaigns represent not only a means of confirming expectations from model predictions, but perhaps more importantly they also serve as the principal means of establishing pollutant trends and verifying expectations from estimated emission changes.

Global Change and Air Quality (Chap. 11): Climate forcing associated with greenhouse gases and climate-affecting particles adds complexity to the multipollutant character of air quality management. Climate change has impacts on air quality management, both in assessment of current air quality conditions relative to past conditions and in projection of air quality in future years (e.g., IPCC 2007). As a result of these projected changes, air quality management policies may need to account for climate change as another degree of freedom in characterizing the consequences of air pollution. Both Canada and Mexico have addressed the climate change issue, and have committed to carbon dioxide reductions as part of current international commitments. Recent judicial and legislative actions in the U.S. (e.g., U.S. Supreme Court [U.S. Supreme Court 2007], and the 2007 Energy Independence and Security Act) have increased domestic attention to possible regulation of greenhouse gases beyond current voluntary programs. Thus air quality management in North America is viewed by many to embody future reductions in greenhouse gases as a part of overall air quality goals.

Changes, Trends, and Accountability (Chap. 12): Some tools for addressing multipollutant air quality management are in use; representative examples of their application that illustrate linkages between pollutants, exposure indexes and effects are discussed in this chapter. These representative examples illustrate the strengths and weaknesses of current methods supporting management actions.

Toward Risk- and Results-Based Multipollutant Air Quality Management—What's Next? and Conclusions and Recommendations (Chaps. 13 and 14): Conclusions regarding the state of knowledge available to support the transition toward multipollutant air quality management are derived from each topic area chapter. Information needed in each of the topical areas to address risk assessment, management, and accountability in a multipollutant approach is identified in terms of the multi-level transition model proposed in this assessment.

Recommendations focus on both the motivation for transitioning to a multipollutant air quality management approach, as well as the research and data collection requirements to forward this transition. The recommendations also suggest activities that will enhance the ability to conduct accountability evaluations to improve the effectiveness of both single and multipollutant air quality management approaches.

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Chapter 3
Decision-Making Framework for Air Quality Management

George M. Hidy, Jeffrey R. Brook, Kenneth L. Demerjian, Luisa T. Molina and Richard D. Scheffe

This chapter sets forth a decision-making framework for multipollutant air quality management in North America that includes risk assessment and accountability. The chapter begins with a summary of today's air quality management structures in Canada, the United States, and Mexico including current capabilities and applications of measuring accountability. The chapter then introduces the elements of multipollutant air quality management; these represent a transition from the present orientation toward single pollutants to risk- and results-based multipollutant management.

3.1 Multinational Perspective

Air quality management systems across North America are founded on a pollutant-specific approach that is based on ambient air quality standards (or goals) for criteria pollutants (which are set to protect human health and welfare), implementation efforts for reaching these standards, hazardous air pollutant[1] programs for reducing emissions, exposure and risks associated with hazardous pollutants, and compliance and enforcement activities for ensuring that the goals and standards are met. In this context, welfare issues include material deterioration, acid chemical deposition and its influence on terrestrial and aquatic ecosystems, and visibility impairment.

The current applicable laws, regulations or guidelines reflecting Canadian, U.S., and Mexican clean air commitments are summarized in Table 3.1 and in the following discussions.

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[1] The terms criteria pollutant (CP) and hazardous air pollutant (HAP) have specific definitions in the United States; definitions of these terms as well as the Canadian and Mexican air toxics are found in the List of Terms.

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Table 3.1 Current air quality management and supporting practices for North American nations. (After NARSTO 2000)

Canada	Mexico	United States
Federal Government		
Development of NAAQO[a] and toxin standards Participation in control strategy design and permitting of facilities for emission management Air quality modeling Air quality monitoring Control strategy design Set transportation and energy policy Set vehicle and fuel standards Manage transboundary issues Conduct research and assessments	Promulgation of air quality objectives, including climate alteration initiatives Air quality modeling Control strategy development Permitting for facilities for emission management Air quality monitoring support Enforcement of management objectives Health and ecological research	Promulgation of the NAAQS and air toxics regulations Development of implementation guidance, including SIP oversight SIP review and designation of non-attainment areas National emission controls on vehicles, fuels, large point sources, etc. Air quality modeling Air quality monitoring Enforcement Address international issues, including transboundary pollution Conduct research and national assessments
Provincial, State and Local Governments		
Participation in the NAAQO development Participation in control strategy design and permitting of facilities for emission management Air Quality modeling and monitoring Enforcement Research	Control strategy development Air quality modeling and monitoring Permitting of facilities for emission management Enforcement Research	Develop and promulgate complementary standards to federal mandates Control strategy development Permitting of facilities for emission management Air Quality modeling and monitoring Enforcement Research
Non-Government Organizations—Industry		
Implementation of emission controls Participation in control strategy development Research	Implementation of emission controls Participation in control strategy development Research	Implementation of emission controls Participation in control strategy development Research
Academia & Other NGOs		
Research Participation in control strategy development Advise future changes in demographics etc. Seek individual control actions Educate and promote stakeholder involvement	Research Participation in control strategy development Advise on changes in demographics, etc. Educate and promote stakeholder involvement	Research Participation in control strategy development Advise on changes in demographics, etc. Review and comment on federal and state-local programs Educate and promote stakeholder involvement

[a] *NAAQO* National Air Ambient Air Quality Objectives. Note in one case, Canada has designated fine particulate matter a toxic species, and thus it is governed by an ambient standard

3.1.1 The U.S. System

Air quality management in the United States currently follows the provisions of the 1970 federal Clean Air Act (CAA) and its amendments in 1977 and 1990, as summarized in Text Box 3.1. The CAA focuses on improvement of public health and welfare through reduction of exposure to CPs (carbon monoxide, sulfur dioxide, nitrogen oxides, ozone, particulate matter and lead) and the 187 designated HAPs. In the case of ozone, multipollutant emission reductions of precursors (nitrogen oxides and volatile organic compounds) have been found to be necessary. In the case of particulate matter, not only are direct emissions of particles controlled, but multipollutant precursors involved in particle formation are addressed, including sulfur dioxide, nitrogen oxides, certain volatile organic compounds, and ammonia.

Text Box 3.1 The U.S. Air Quality Management Structure

Current air quality management practice in the United States is largely driven by legislative direction provided in the 1990 Clean Air Act Amendments (CAAA), combined with earlier legislation from 1967, 1970, and 1977. Titles I–IV of the CAAA establish a mix of emission and air quality goals focused on single pollutants classified as CPs and HAPs, with responsibilities distributed and shared among federal, state, local and tribal governments. Currently two dominant source sectors, transportation (Title II) and energy generation (Title IV), are treated explicitly although with different objectives. Protection of human health is a dominant goal throughout the CAAA, though Title IV sulfur dioxide and nitrogen oxide emission reductions were designed to limit watershed acidification in the eastern United States. While the CAAA provides authority for considering secondary welfare effects on aquatic and terrestrial systems stated in terms of air quality related values, more substantive efforts beyond human health objectives have been directed to visibility impairment in pristine areas.

Major components of the U.S. air quality assessment and management framework are these regulatory, policy, research, information collection, and assessment programs:

- National Ambient Air Quality Standards (NAAQS) review and setting process.
- Development of federally initiated national rules to assist in attainment of NAAQS and other objectives, including emission standards, emissions cap and trade programs, new source performance criteria and review for stationary sources, and vehicle performance standards; definition and application of best available control technologies, maximum achievable control technologies (MACT), and lowest achievable control technologies.

- Development of State Implementation Plans (SIPs) and regional haze programs by individual states and interstate organizations to achieve goals for ambient air quality.
- An overarching HAPs management program charged with developing emission-based reductions (e.g., MACT) and risk based e.g., residual risk) standards for HAPs (after application of MACT) for quantifying individual risk.
- An accompanying technical infrastructure including scientific research, air quality monitoring networks, emissions inventories and models.
- Consideration of local, regional and trans-national boundary measures for air quality management.

With the amendments, the CAA also provides for national programs to preserve air quality-related values, including visibility and vulnerable ecosystems in pristine areas such as the national parks and wilderness areas. Through Title IV of the CAA, additional provisions protect vulnerable ecosystems from exposure to deposition of acid-forming gases.

Administratively, through provisions for establishing and enforcing the laws governing emission reductions, the CAA has established a substantial shared infrastructure at the federal, state, tribal and local level. Emission standards for pollutant sources such as on-road vehicles and electricity generation largely fall under the jurisdiction of the federal government, while for sources such as industrial, commercial, residential, and fugitive emissions jurisdiction is shared among federal, state, tribal and local governments.

The U.S. system basically relies on ambient standards as a means of human health and welfare management, along with emission standards for sources. The ambient standard setting process for CPs involves an initial review of each pollutant, followed by periodic review and promulgation of revised standards. Each standard includes a concentration level and an oxidant indicator species like ozone, an averaging time for exposure, a statistical form (such as the number of allowed exceedances or the occurrence frequency), and the associated measurement method. The standard setting and review process is complex and can require a number of years to achieve. Management of HAPs relies on emission standards by source to deploy maximum achievable control technology with review to ensure that the maximum individual risk from exposure to a HAP is below an acceptable level.

Once the standards are established, monitoring data are acquired for three years to determine areas where ambient conditions exceed the standards. States are then required to prepare state implementation plans (SIPs) to indicate how they will achieve the standards in affected areas. Current practice uses a “weight of evidence” process (e.g., EPA 2007a) using measurements and air quality modeling to direct the geographic areas to attainment of the standards by certain dates, or to ensure maintenance of air quality using the standards as a metric in different areas.

Many of the specific provisions of the U.S. system are deemed technologically forcing in that they require major technological modifications to reduce pollutant emissions through modification of process technology or post-process control technology. Examples of post-process technology include stack emission reductions through scrubbers, catalytic reactors or filters. For transportation, modifications in combustion technology combined with devices to control exhaust emissions have been deployed since the 1970s. The technology forcing elements mainly derive from federal and private sector expertise, which has introduced over a period of time the necessary technologies to achieve emission requirements for new sources and retrofit of existing sources.

3.1.2 The Canadian System

The Canadian air quality management system addresses CPs and other air emissions via shared authority between the federal government, provinces, and territories. The Canadian Constitution empowers the provinces to make laws governing property and civil rights and gives them jurisdiction over much of the land and resources within their boundaries. The federal government's principal framework for protecting the health of Canadians and the environment with respect to air pollution is the Canadian Environmental Protection Act (CEPA) 1999 (see Text Box 3.2). The CEPA 1999 federal obligations and authorities include research and information collection, trans-boundary and international issues, vehicle and fuel regulation, and regulation and management of toxic substances. Provincial and territorial responsibilities for managing air pollution primarily involve the development, implementation, and enforcement of regulations and standards to control emissions from industrial, commercial, and other sources of air pollution. Provinces and territories do this largely through licensing, permitting, monitoring for individual facilities, and stipulating emission limits and other environmental protection requirements.

Text Box 3.2 The Canadian Air Quality Management Structure

The CEPA 1999 and its updates provide the federal government a clear jurisdiction to regulate air pollutants in order to protect the environment and the health of Canadians. The primary elements of the Canadian structure include establishment of national standards for emissions from vehicles, fuels, and products; addressing Canadian sources that contribute to international pollution; controlling production and release of toxic substances; and establishing national objectives, guidelines, and codes of practice to protect the environment.

Provincial permitting systems for stationary sources of air pollution are the primary mechanisms for implementing air quality goals and objectives in Canada. Limits on individual facilities are established based on both ambient levels and technology standards. Requirements can vary significantly from province to province but all require pre-construction approvals and operating permits for what are considered as significant new, or modified stationary sources of air pollutants and generally contain three elements: emission limits, expiratory provisions, and monitoring and reporting requirements.

Compliance and enforcement activities in most jurisdictions involve ambient air analysis in the vicinity of the permitted operation. In some instances the permitting authorities will require the proponent itself to conduct and sponsor ambient air monitoring, though in most cases the provincial authority takes responsibility for the conduct and cost of such activities.

In November 2005, Ontario's Regulation 419, "Air Pollution—Local Air Quality" came into effect, updating the regulatory framework (Ontario Regulation 346) The new regulation sets new and updated air standards for 40 harmful pollutants (96 air standards in Regulation 346); updates air dispersion models; and implements a risk-based approach to set and implement air standards. Thus, the new regulation includes a regulated decision-making process to improve the implementation of air standards. Provincial air quality standards are set to protect against health and environmental impacts. Ontario has developed the risk-based decision-making process to manage risk when a facility has difficulties (economic or technological) meeting Ontario's Point of Impingement standards.

The federal, provincial, and territorial governments work together under the Canadian Council of Ministers of the Environment and the Canada-Wide Accord on Environmental Harmonization. Ministers (except Quebec) signed the Canada-Wide Standards for Particulate Matter and Ozone in June 2000, committing to set out an implementation plan for meeting the standards. Like other agreements on Canada-Wide Standards, this plan is based on the principle that responsibility and actions will be assumed by the best-situated order of government.

Multipollutant concepts are becoming a more formal part of the federal process. In April 2007, the Canadian government announced its Regulatory Framework for Air Emissions. The Regulatory Framework for Air Emissions sets reduction targets for emissions of greenhouse gases and air pollutants from all major industrial sources in order to provide a nationally consistent level of protection for the health of Canadians and their environment. The government is currently in the process of finalizing the air pollutant targets for all major industrial sectors for NO_x, SO_x, VOCs, and particulate matter. Targets for air pollutants will come into force in Canada as early as 2012.

Providing coordinated requirements for these air pollutants and greenhouse gases will allow firms to make cost-effective decisions to maximize synergies in reducing emissions. An emission trading system for SO_x and NO_x will be introduced to allow companies to choose the most cost-effective way to meet their regulatory reduction obligations. Trading will be restricted in areas that have poor air quality to help maintain a level of local or regional air quality. In addition, the regulations for industrial air emissions will be reviewed every five years in order to assess progress in reaching emission reduction objectives.

The Canadian government regulates the fuel efficiency of cars and light duty trucks and will develop additional regulations as needed to continue to align Canadian vehicle and engine air pollutant regulations with world-leading standards of EPA and to implement initiatives to ensure a more streamlined and efficient regulatory system. In implementing the Regulatory Framework, the federal government will continue to work in partnership with provinces and territories to promote approaches that avoid unnecessary duplication of effort.

To address ecosystem concerns, Canada has adopted a metric for acid deposition which assumes that a coarse threshold exists (a critical load) for acid forming species, below which either minimal or no cumulative ecological damage results in vulnerable aquatic systems. This loading has been used to determine a “target load” to achieve levels of deposition below those believed to be dangerous to certain vulnerable ecosystems (see also Chap. 6).

Air quality issues between Canada and the United States have been addressed through the Trail smelter issue in the 1930s, the Great Lakes initiatives, and through agreements relating to the reduction of ozone, PM_x, certain HAPs, and acid deposition from transport across the border, all of which involve multipollutant considerations (examples are discussed in Chaps. 6 and 12). Analogous agreements have been developed between Mexico and the United States through NAFTA for the border communities and for large stationary sources in northern Mexico.

3.1.3 The Mexican System

The regulatory framework for Mexico’s air quality program is summarized in Text Box 3.3. Mexico relies on federal and local indexes as objectives or targets, similar to Canada’s air quality objectives for CPs. Mexico’s focus has been largely on ozone and PM, especially in Mexico City and the Valley of Mexico. Other major urban areas such as Monterrey and the U.S.-Mexico border cities also are considered in regulations, along with major stationary sources located in parts of non-urban Mexico. Reductions in emissions of CPs have been negotiated with stakeholders including both heavy industry and transportation components. These emission reductions appear responsible for the observed improvements in air quality that have been documented in recent years, particularly in Mexico City (DDF 1997). Important progress has been recorded in the motor vehicle sector, including introduction of unleaded gasoline in the 1990s, in SO_2 and NO_x reductions, and control of PM through reductions in fugitive dust and other sources in the urban and U.S.-Mexico border areas.

Text Box 3.3 The Mexican Air Quality Management Structure

Title IV of the General Law of Ecological Balance and Environmental Protection (Ley General del Equilibrio Ecológico y la Protección al Ambiente—LGEEPA) provides the regulatory framework for Mexico's air quality program. According to this law, ambient air quality standards (which are roughly comparable to U.S. standards) are established by the Secretariat of Health (SS) and the Secretariat of Environment and Natural Resources (*Secretaría de Medio Ambiente y Recursos Naturales—SEMARNAT*) is the federal authority responsible for regulating emissions, with the main objective of protecting human health and complying with the ambient air quality standards.

SEMARNAT regulates stationary sources under federal jurisdiction, issues all regulations pertaining to these sources (Normas Oficiales Mexicanas—NOMs) and implements all enforcement and oversight activities pertaining to air pollution control. NOMs specify maximum allowable limits for stack emissions due to combustion and some process emissions from point sources, as well as mobile source emissions. These NOMs represent minimum criteria, and states may implement more stringent standards.

According to federal law, local (i.e., state and municipal) authorities are entitled to regulate and control point sources not included in the sectors regulated by SEMARNAT. They are also responsible of enforcing federal NOMs on mobile source emissions (i.e., they are responsible for establishing inspection/maintenance programs to check compliance of mobile sources registered within their jurisdiction). Hence, all states including the Federal District have established local environmental protection and management agencies for air pollution prevention and control. States have also issued their own environmental laws and regulations, which are largely based on the LGEEPA.

Air quality management activities in large cities have aimed to include most of the following six steps of an integrated approach: (1) developing a bottom-up emission inventory; (2) establishing an air quality monitoring network; (3) modeling the dispersion and transformation of pollutants in the urban atmosphere; (4) carrying out exposure assessment studies to determine the activities and groups of the population that may be at higher risk; (5) developing/applying dose-response functions to estimate the likely health effects, and (6) assessing the approximate cost incurred by society due to the morbidity and mortality caused by air pollution.

3.1.4 Accounting for Global Change and Greenhouse Gases

Anthropogenic climate change is a global-scale environmental issue having significant implications for air quality management. It results from the accumulation of radiation absorbing greenhouse gases[2] and radiation absorbing and scattering particles in the atmosphere, which can also affect climate through their effects on cloud properties and processes. Attempts to mitigate climate change could result in multipollutant air quality management actions to reduce emissions of climatically active gases and particles. Some of these climatically significant gases and particles are also designated as regulated air pollutants or precursors to air pollutants and others share common sources with these pollutants. Both Canada and Mexico are signatories to the Kyoto Protocol (http://unfccc.int/kyoto_protocol/items/2830.php), and under the protocol Canada has agreed to take actions to reduce national greenhouse gas emissions to specified targets within a specified timeframe.

Until recently, the United States has relied on voluntary actions to reduce greenhouse gas emissions, while it has explored the role of technology development in emission reduction. The 2007 Energy Independence and Security Act, however, mandates greenhouse gas emission reductions from the transportation sector through renewable fuel standards (which require that life cycle greenhouse gas emissions for biofuels be at least 20% lower than the gasoline or diesel they replace) and through improved fuel efficiency. Some state and local governments have also begun taking actions designed to reduce greenhouse gas emissions.

A U.S. Supreme Court decision (U.S. Supreme Court 2007) will have a significant impact on the regulatory dynamic in the United States with regard to greenhouse gas regulation. The decision, which specifies that greenhouse gases, particularly CO_2, are covered under the CAA as an air pollutant, will increase pressure for some form of U.S. regulation of greenhouse gas emissions. However, climate change has become an increasingly divisive political issue in the United States. It is not at all clear how the U.S. will be dealing with this issue, at least in the short term. Nevertheless, as all three countries of North America develop greenhouse gas management strategies, they will likely consider this issue within emerging energy policies as part of an overall multipollutant management strategy.

3.2 Measures of Progress (Accountability)

Accountability is the process of demonstrating that actions taken to improve air quality have had the desired effect. Formally, it is implemented through a series of steps frequently called the accountability chain. These steps incorporate various measurements and analyses for determining whether

1. The management action was implemented as designed and the expected emission reductions have taken place.
2. The actual or estimated emission changes resulted in the expected changes in ambient concentrations or deposition.

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[2] Greenhouse gases involved in climate forcing include carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), ozone, and certain halocarbons. Climate forcing also is associated with fine particles in the atmosphere.

3. The changes in ambient concentrations or deposition have resulted in reductions in exposure of humans or ecosystems to the pollutants in question.
4. These reductions have led to improved public health or reduced damage to sensitive ecosystems.

However, despite forty years attention to air pollution reduction a formal demonstration of the effectiveness of these actions—from implementation to effects—has yet to be completed.

Measures of progress toward cleaner air are certainly reported in North America (e.g., EPA 2008). These measures usually embody a qualitative comparison of estimated changes in emissions over multiyear intervals with changes in the ambient concentrations of pollutants. Changes in human exposure are tracked using ambient concentration as a proxy. Exposure to ecosystems is identified with ambient concentrations or with deposition of chemicals (like acids) to vulnerable aquatic or terrestrial ecosystems. Except for the case of lead, which is described in Text Box 3.4, similar demonstrations that reductions in emissions have resulted in reductions in human exposure to pollutants and improvements in health have not been made until recently. These demonstrations include epidemiological studies for $PM_{2.5}$ reductions (e.g. Laden et al. 2006; Pope et al. 2009) and so-called intervention studies for $PM_{2.5}$ (see also Chaps. 5 and 12).

Text Box 3.4 The North American Lead Story

Airborne lead is often cited as a major success story for tracing the reduction in emissions through exposure to a measure of biological change (e.g., NARSTO 2000; Needleman 2000). Lead became a CP in the United States in 1978, the only particulate species so designated to date. This determination was based on the documentation of neurotoxic effects of lead, particularly in children. Subsequent reduction in ambient lead concentrations came principally from the elimination of lead from gasoline and emission reduction from the paint industry and other stationary sources. About the same time, Canada eliminated lead from gasoline in favor of the use of alkyl manganese as a substitute (Canada has since removed this anti-knock agent from its gasoline supply). In the 1990s, Mexico also eliminated alkyl lead additive from its gasoline, so that gasoline sold in North America basically contains no lead. Subsequently, ambient lead concentrations measured in all three countries have declined dramatically, and they have been reflected in reductions in the exposure biomarker, blood lead, in the three countries. Recently, EPA has reported a direct relationship of blood lead with neurotoxicity in children, including declines in IQ (EPA 2007b). The epidemiological and toxicological evidence reported by the EPA indicates that environmental lead concentrations should continue to be reduced to further reduce the risk of lead poisoning. The apparent proportional reduction in neurotoxicity with ambient lead and personal exposure marked by blood levels infers a benefit from risk reduction through an identifiable biomarker for a pollutant.

The simplest accountability demonstration is to determine whether improved air quality is associated with reduced primary pollutant emissions, and there are a number of cases for which this has been done. For example, reductions in SO_2 and NO_x emissions resulting from the U.S. and Canadian acid rain programs and the EPA's 1997 NO_x SIP Call have resulted in systematic reductions in ambient concentrations of SO_2 and NO_x throughout the eastern United States and eastern Canada, as well as reductions in airborne sulfate and sulfate deposition. However, it is more difficult to relate reductions in secondary pollutants, such as ozone, (particulate) nitrate, and the organic carbon components of particulate matter, to reductions in their precursor emissions. Nevertheless, EPA has linked ozone improvements in the eastern United States to NO_x emission reductions achieved through the NO_x SIP Call (EPA 2007c; see also Chap. 12).

It is more difficult to show that actual or estimated emission changes have resulted in the *expected* changes in ambient concentrations or deposition (e.g., NARSTO 2005). Differences between modeling results and ambient measurements of species from different sources can occur for several reasons. Some of these include inaccurate emission projections, inaccuracies in other model inputs and the parameterization of chemical processes and pollutant losses, and the inability to complete a material balance for species such as nitrogen oxides or carbon being tracked either with measurements or with calculations.

Difficulties in comparing model predictions with results also arise from changes over time in methods for estimating emissions. Differences between estimated and actual changes may also occur if air quality management strategies were based on poorly understood scientific principles, and as such, focused on reducing the wrong pollutant. An example would be reducing local emissions of VOCs rather than NO_x as a strategy for urban ozone reduction. In cases such as this, implementing an accountability program in concert with implementation of an air quality management action could provide early detection of such problems and enable corrective actions to be taken earlier than otherwise. In still other cases, air quality impacts from emission changes may be obscured by meteorological variability that results in a range of fluctuations in pollutant concentrations spanning a few years and affect monitoring observations taken at a fixed site (e.g., Rao et al. 1997).

A specific example of the consequences of incorrect emission projections is the differences between the actual and expected benefits resulting from the introduction of new technology to reduce emissions of carbon monoxide and related hydrocarbons from light duty vehicles. In this case, two key errors were made in the emission estimates. One, projection of the benefits that new technology would have in reducing emissions was not realized; the projections did not anticipate the influence of high-emission vehicles and their dominant effect on air quality. Two, the emission projections missed the growth of on-road vehicle-miles-traveled or volume of fuel used, especially in major metropolitan areas like southern California and the Atlantic Coast megalopolis. Because of these factors, CO and VOC reductions were lower than projected and consequently urban ozone reductions were lower than anticipated in the 1980- early 1990s period (e.g., NRC 1991). A more appropriate indicator of the effects of the CO and VOC emission reductions might have been a measure of emissions per vehicle or fuel volume used (determined by CO_2 observation with CO and VOC). These types of emission indexes help to identify whether a particular control measure is effective, and separate the impact of controls from the impacts of changes in population behavior.

The most difficult accountability demonstration is to show that actual or estimated changes in emissions have resulted in the expected health or ecosystem benefits. In the contemporary decision-making process, the benefits of an anticipated air quality management action are estimated by computing expected reductions in ambient concentrations based on projected emission reductions. The expected reductions in ambient concentrations then drive a health impact analysis, which combines the changes in ambient concentrations with population data, baseline health information, and information on pollution-related health effects to estimate expected reductions in pollution-related health effects (e.g., HEI 2003). Verifying that these health benefits were achieved has proven to be elusive even for single pollutants. Detecting the effect of reductions in pollution on human health using ambient concentrations as the surrogate for exposure is difficult to achieve using existing statistical methods where the change is gradual and the signal to noise ratio is small. While research continues on this matter, we must conclude that completing all four steps in the chain of accountability will remain difficult for the foreseeable future. In the meantime, the path to achieving accountability for air quality management actions will continue to rely on a weight-of-evidence approach. In the recent past, this approach has given greatest weight to emission trend estimates and ambient air quality changes to evaluate progress to achievement of national goals, supplemented with modeled exposure, risk, and effects information. Corroborating case studies such as emission intervention investigations, and surveillance of ecosystem changes will be the principal means of evaluating the effectiveness of single or multipollutant air quality management strategies, although recent advances in linking health outcomes with direct measures of personal exposure (e.g., in the ongoing MESA-Air study[3]) may improve the ability to directly measure effectiveness.

3.3 A Multipollutant Management Outlook

Advances in knowledge since the 1960s have demonstrated the complexity of interactions between multiple atmospheric contaminants. This knowledge combined with progress in characterizing the environmental stresses brought about by emitted pollution and atmospheric end-products continues to expand, with perhaps the latest being identification of issues related to the potential interactions between climate and air quality. Superimposing the potential for a hierarchy of health and welfare effects on the current air quality management framework suggests that alternative approaches to air quality management could be considered (NRC 2004). Much of

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[3] For information on the Multi-Ethnic Study of Atherosclerosis (MESA) Air Pollution Study, see http://depts.washington.edu/mesaair/.

the existing framework in North America could be adjusted administratively to improve the efficiency and effectiveness of achieving multipollutant air quality management objectives.

One way to increase the efficiency of the present management process is to deploy emission control technologies that reduce multiple pollutants. These types of technologies have been developed for mobile sources and have been part of light duty vehicle technology in the United States since the 1980s. Reductions in sulfur in fuels coupled with advanced three-way catalyst exhaust converters result in continued reductions in NO_x, VOC, CO and SO_2 emissions. For coal- or oil-fired power plants, addition of effluent scrubbers for the removal of SO_2 also reduces mercury emissions. Recently, energy efficiency approaches such as demand-side options for reducing fuel use have reduced pollutant emissions. While opportunities for deploying technologies for reducing multiple emissions exist, one must take care to ensure that their use does not increase other pollutant emissions. Two examples of this problem are increased ammonia emissions associated with motor vehicle catalytic converters and ammonia slip from selective catalytic reduction of NO_x from stationary sources.

Moving beyond multipollutant emissions reduction to a *risk-based* multipollutant air quality management strategy might require changes to the existing laws governing air pollution. The argument for evolving air quality management practices toward a multipollutant approach is based on both technical and administrative considerations. Technical concerns relate to the fact that most sources do not emit just one pollutant, but emit several pollutants in varying effluent concentrations. Upon entering the ambient air, these mixtures of emissions are subjected to the same physical processes of dispersion and disposition in the atmosphere, but experience a variety of chemical transformations. The physical and chemical processing of emissions in the atmosphere typically results in a complex diluted mixture of primary emitted species and their reaction products. These mixtures are space and time dependent and are important in determining multipollutant exposures. Receptors are stressed through encounters with these mixtures of gases and size differentiated particles that vary with temperature, humidity and solar radiation.

The regulated CPs and HAPs represent indicators of exposure to complex pollutant mixtures. Today's administrative practices recognize some elements of the effects of multiple pollutants, but they have not accounted for all of the potential stresses encountered. In past practice, environmental stresses by pollutant have been dealt with independently, and not as an interdependent set. Inefficiencies have developed over time, which include in the United States mismatches in the calendars for implementation of regulations, as in the case of SIP development and approval for the ozone and $PM_{2.5}$ national ambient air quality standards. While clean air administrative goals are implemented in different ways by Canada, the United States, and Mexico, they all have the potential for addressing multipollutant issues more efficiently.

The conceptual principles of environmental protection outlined in the NRC (2004) report form a basis for proceeding with an investigation of possible improvements to the current air quality management systems. In particular, for the

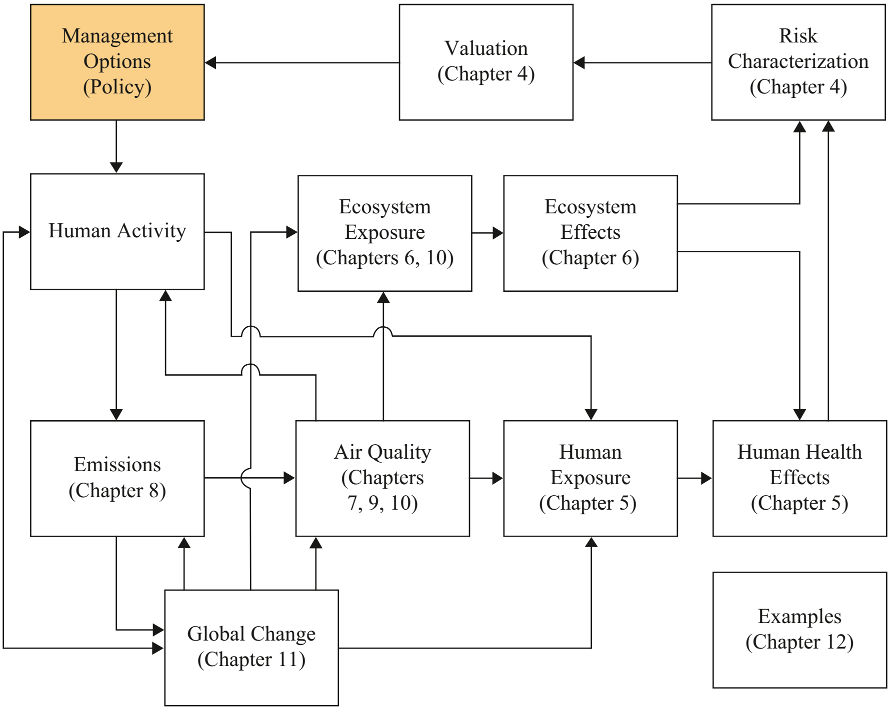

Fig. 3.1 Schematic diagram of components of risk analysis leading to multipollutant air quality management options. Each component shown in the diagram has a counterpart in the chapters of this assessment

United States at least, the CAA and its amendments set a broad governing structure for applying these principles, not only for single pollutants but for multipollutants. As in the past, identification of environmental hazards and goal-setting represent an important starting point for an assumed air quality management approach (see Fig. 3.1).

3.3.1 A Proposed Agenda for Transition

Changing national structures to accommodate a multipollutant management approach responding, for example, to the NRC (2004) recommendations cannot occur in a sudden transition from current practice to a new framework. From a socio-political standpoint, the existing laws and administrative procedures, including the CAA, have evolved in response to many years of experience and litigation. Formalization of a risk-based cycle (Fig. 3.1) within a single pollutant management paradigm will take time and will require incremental change rather than a sudden abandonment of current practice. This is especially the case in the United States where the air pollution management infrastructure has built up around the CAA approach since 1970, and where existing single pollutant programs are viewed as having been largely successful in reducing pollutant emissions while maintaining economic growth. The burden involved in reopening clean air legislation serves as an additional barrier to implementation of large scale changes in the U.S. approach. However, a growing concern about management of climate-forcing emissions may represent an opportunity to revisit the current air quality management paradigm as governments seek ways to reduce greenhouse gas emissions while still improving air quality.

In order to assess the technical challenges of moving to risk- and results-based multipollutant air quality management the authors of this assessment postulated a four-level transition from current air quality management practice to a full risk-based multipollutant approach. This postulated transition allowed the authors to examine which aspects of a risk- and results-based multipollutant approach might be implemented now or in the near future and which would require more technical development.

Level 1. A Strict Single-Pollutant Perspective with the Focus on Attainment of Individual Ambient Standards. In current regulatory administrative practice, management approaches are guided by single pollutant goals without formal consideration of coincident or cumulative benefits or tradeoffs. In principle, the current underlying information and assessment structure is capable of addressing multiple pollutant consequences of emission strategies. However, this structure has been used only to determine, for example, an efficient pathway to attaining a specific ambient standard or objective (e.g., ozone or $PM_{2.5}$) in a designated management area and time frame. Elements of a supporting infrastructure include multipollutant atmospheric modeling and emission inventory systems. Advances in air quality modeling include simultaneous treatment of CP gases, precursor gases, particulate mass (and composition), and some HAPs, including mercury. In principle, the calculations allow for quantification of changes in atmospheric concentrations and deposition of many different pollutants associated with single or multiple changes in emission precursors. If the emissions are known over a period of years, backcasting and forecasting with the models can yield an estimate of trends and a projection of future conditions for comparison with observations of ambient concentrations. Air quality model results are available to the exposure and effects communities for application to risk assessment.

Level 2. Attainment of Standards for Individual Pollutants, but with Increasing Attention to Co-benefits Attainable Through Coordinated Emission Reductions. A first-step modification of previous approaches would use multipollutant analytical tools driven by a primary single-pollutant goal, combined with a parallel, secondary interest in maximizing additional coincident benefits associated with collateral emission reduction of several pollutants within the principal target. For example, advances in air quality modeling enable estimation of the influence of emission precursor reductions across pollutants such as ozone (photochemical oxidants), PM, and HAPs. Thus, coincident benefits derived for HAPs or PM based on a strategy designed for ozone can be assessed, as well as other options (e.g., coincident ozone reduction benefits from a PM oriented strategy). Conceptually, alternative emission strategies can be evaluated on the basis of proposed strategies maximizing primary benefits by single CPs or HAPs, combined with collateral benefit beyond meeting the primary objective. This analysis is being done informally within EPA, but it could readily be formalized or required in terms of a risk- and results-based administrative framework, provided confidence exists in the inputs to a multipollutant risk minimization scheme.

Level 3. Management Decisions Based on Achieving Greatest Risk Reduction Based on Single-Pollutant Exposure-Dose-Response Relationships. A variety of emission reduction strategies can be developed to meet simultaneously several established air quality (and deposition) targets by considering in parallel several pollution targets without constraining the analysis to a single target decision. Imbedded in *Level 3* is the concept of trade-offs to prioritize actions that will be most important in terms of risk reduction. This approach would require that target goals (e.g., air quality standards or benchmark concentrations associated with an agreed-upon risk threshold) be associated with each pollutant in a formal, collective optimization of emission reductions within multiple time constraints and exposure levels. Such a formal optimization analysis would require a complex integrated risk assessment model, given contemporary knowledge about single pollutant targets. Such models can be or have been constructed with conventional optimization schemes when the single pollutant risk-benefit data are available or can be constructed.

Level 4. Management Decisions Based on Achieving Greatest Risk Reduction Based on Multipollutant Exposure-Dose-Response Models. *Level 4* encompasses a variety of possible emission reduction strategies, such as tradeoffs or a net risk reduction or maximum benefit yield without one pollutant target (or effect) constraining the analysis. Risks (and benefits) would be determined on a pollutant within a multipollutant combination, and could include synergisms if they exist. The approach would require availability of exposure-response functions (and ideally, valuation measures) for pollutant exposures of interest, designated as groups or mixtures. By incorporating overall risk reduction, *Level 4* allows for a robust and comprehensive treatment of the impact of strategies for human and environmental health protection, relative to specified target goals for emission and subsequent ambient exposure reduction. *Level 4* would recognize that human health and ecosystem effects are subject to the interactive influences of aggregate exposures. These may range from a synergistic increase to a compensating interaction that differs from a simple additive compilation of pollutant by pollutant exposure-response relationships and recognizes synergism from multiple exposures.

3.3.2 Evolving the Air Quality Management System

Levels 1 and *2* approximate the current status of air quality management, particularly in the United States. Informal application of risk assessment modeling for parallel CP management plays an internal role at a policy analysis level, but in most cases does not significantly influence the administrative design of current compliance strategies. As management strategies develop with greater advances in knowledge, risk assessment should become increasingly important in the evaluation of emission reduction polices. Even with improved knowledge and models for risk analysis, challenges remain in incorporating the results of these analyses into formal decision-making processes, partly due to the difficulty of clearly communicating the results of these risk analyses to decision-makers, especially when there are large uncertainties associated with the estimated risks.

In principle, a *Level 1* assessment as currently practiced can address certain multipollutant issues. Since decisions also are based on the expected improvements in human and ecosystem health with exposure reduction, the actual effects are evaluated through weight-of-evidence approaches. This is particularly true for the widely known multipollutant complex incorporated by particulate matter. Hence, regardless of a movement toward a multipollutant paradigm, there is a need for new knowledge of effects, including exposure-response relationships for single pollutants.

At present, developing strategies for air quality management are increasingly directed toward achieving air quality management at *Level 2*, including some experimentation in methodological protocol. However, questions adjunct to risk assessment need to be addressed. For example, consideration could be given for a strategy to address certain combined issues:

- Minimizing unintended collateral adverse outcomes (e.g., elevated ozone in urban cores due to reduced NO_x available for reaction with ozone and trade-offs associated with changes in NO_2 [also Chap. 12]).
- Achieving specific goals for species from atmospheric chemical reactions (e.g., meeting a PM standard [contains a large fraction of secondary particles] in addition to ozone).
- Achieving differential reductions considering all sources (relative to a current year base case) across all quantified species of interest (CPs, HAPs and species of concern for chemical deposition).
- Achieving an optimum overall risk reduction (implying that a risk-based weighting incorporating adequate exposure and effect information is available for estimated concentration or [deposition] changes on a species basis).
- Combining elements of such considerations with practical technology adaptations, and cost effective control technology applications.
- Providing the underlying data and tools to allow decision-makers to make choices, allowing differentiation by priority for reduction of some pollutants relative to others.
- Providing data and tools to enable decision-makers to make decisions about acceptable risks, and thus determining when remaining emission levels are acceptable, while others need to be addressed.

Beyond *Levels 1* and *2*, the strategy of implementing an expanded management strategy is uncertain. At *Levels 3* and *4*, a regulatory framework is needed that identifies a clear method for developing targets that combine CPs and HAPs. Targets exist for CPs, based on ambient air quality objectives (standards), and welfare measures such as visibility (in the United States). However, the existence of accepted targets (or benchmarks) is not available generally, or at least is ill-defined for most HAPs (the minimum target in the United States is an individual risk of one in a million for HAP emissions from specific source categories). The targets for chemical deposition, as another example, are also technically ill-defined for lack of extensive dose (or loading)-response data, and are not used in the United States. Canada, on the other hand, relies heavily on these critical load measures for guiding planned reductions in deposition of acidic species. At *Levels 3* and *4*, results quantified by risk assessment for meeting an objective by location, as well as attendant benefits elsewhere (where conditions are below a set air quality objective or reductions in concentrations are greater than an established reduction target) are included in a risk-benefits assessment.

In the U.S. context, for example, efficiencies in air quality improvement could be gained by aligning timeframes for existing regulatory requirements to be compatible across pollutant categories or designated groups, and allowing time for applying complex tools in an iterative fashion to achieve optimization. For example, the assessment efforts underlying an ozone reduction plan could be conducted in parallel to and integral with that for PM, HAPs, and regional haze reduction plan, especially where chemical interactions are known or can be estimated. Actual attainment of a combination of targets would be subject to availability of control technologies, implementation steps, and system response considerations. Sources would be subject to a unified treatment, in an administrative context, of all emission releases to reduce processing associated with multiple or overlapping rules. Examples of progress in this direction include the integration of the ozone and $PM_{2.5}$ strategies of the California South Coast Air Quality Management District (http://www.aqmd.gov), and the approach taken in Georgia (Cohan et al. 2007). EPA also has organized a demonstration of a risk-based optimized strategy for the Detroit metropolitan area (Wesson et al. 2010).

Perhaps the most difficult aspect of developing a multipollutant air quality management framework is the lack of knowledge about effects. At this juncture, a more comprehensive understanding of effects is confounded by the use of multiple endpoints to measure human or ecosystem response. This is further confounded by the difficulties in translating toxicological knowledge into bases for epidemiological interpretation. The existing epidemiological associations between specific pollutants and adverse health effects may reflect responses due to multiple pollutant interactions. Because current air pollution health research is guided by a single pollutant focus, little effort has been devoted to the investigation of multipollutant exposures, particularly synergistic influences. This situation is generally the case for ecosystem stresses as well. A lack of quantifiable relationships supporting interactive effects precludes, at this time, incorporation of multiple pollutant interactions through multivariate approaches, and a formal multipollutant accountability process.

3.3.3 Integrating Multipollutant Air Quality Management with Accountability

Figure 3.2 illustrates the parallels between risk analysis and accountability. On the left are the elements of hazard or risk identification and characterization, which lead to goal setting. The management hierarchy, including the expected outcome of establishing air quality goals and projecting emission reduction requirements or alternatives, is shown in the middle column. The accountability management structure is shown on the right. As the cycle of risk assessment and management is implemented, its periodic evaluation in terms of accountability feeds back information for adjusting the processes of estimating management options and actions to achieve certain outcomes.

The accountability process emphasizes timely evaluation of implementation progress at different levels (e.g., program effectiveness, emission reductions, air quality change, etc.) to ensure that original assumptions are evolving as anticipated. Feedback from the accountability process can be used to modify original program actions as needed. This ideally provides a measure of assurance that elements of an air quality management framework with the greatest uncertainty will be evaluated closely and adjusted to reflect new information as it becomes available. Advances in knowledge, while an accountability capability is developed, drive the achievement of risk- and results-based air quality management as described in *Levels 3* and *4*.

Achieving integration of *Level 3* or *4* multipollutant air quality management with accountability will require the development of additional knowledge and analysis tools. Chapter 13 of this assessment provides a multiyear research and development agenda for achieving these developments. The goals for research and development will continue to support attainment of the CP and HAPs goals established by existing practices. At the same time, modifications in the air quality management process should be explored to incorporate increased use of risk-based assessments that could maximize risk reductions at minimum costs, accounting for known or anticipated interactions between pollutants. In addition, research should be undertaken to foster a credible accountability process (Fig. 3.2). Over the long term, this research and development program would establish the science and technology foundation to support a transition to a risk- and results-based multipollutant air quality management system

Given the conceptual framework discussed in this chapter, let us proceed in the next several chapters to discuss the key enabling technologies available for multipollutant air quality management, beginning with the current status of risk analysis and risk management tools.

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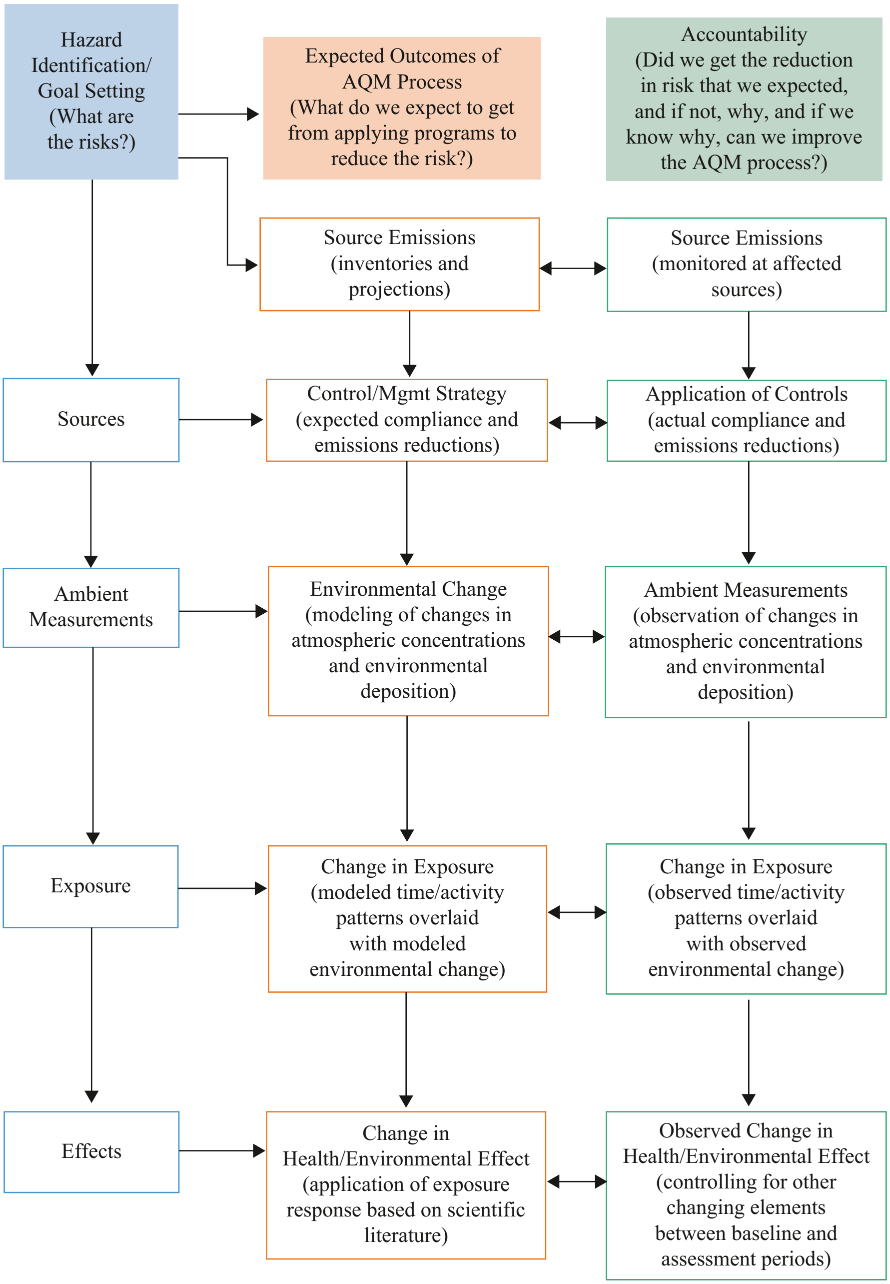

Fig. 3.2 Parallelism between elements of risk analysis and elements of performance evaluation (Accountability) in air quality management practice

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Chapter 4
Risk-Based Assessment and Management Framework

Bryan Hubbell and Chris Frey

The U.S. National Research Council recommends adoption of a multipollutant approach to air quality management that is both risk- and results-based (NRC 2004). Management decisions should be based on minimizing the exposure to, and risk of adverse effects from, multiple sources of air pollution. The success of these decisions would be measured by how well they achieved these objectives. Here, we provide a brief introduction to risk analysis and how it is applied within the current approach to air quality management. Recommendations are made as to how current practice could evolve to support a fully risk- and results-based air quality management system.

Canada, Mexico and the United States generally follow a single pollutant approach to air quality management, e.g., standards are set for individual criteria air pollutants such as NO_x, ozone, and particulate matter (PM), and separate regulations are developed to address air toxics. There are numerous examples in which formal risk assessment methods have been applied to criteria pollutants (CPs) and hazardous air pollutants (HAPs) (EPA 2005, 2006, 2007a). Conceptually, transition from current practice to an integrated multipollutant air quality management strategy would entail:

- Hazard identification with respect to public health and ecosystem protection.
- Assessment of human and ecosystem exposure and response to multiple pollutants.
- Risk characterization of human individual, human population, and ecosystem risks in order to support risk management decision making.
- Reduction of emissions of multiple pollutants and resulting ambient concentrations to minimize exposure risk.
- Assessment of the influence of emissions from local, regional, national, and international sources on exposure and risk.

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- Development of data and tools to support these activities.
- Development of a system for measuring performance of the management system that will assess the effectiveness and efficiency of management actions and dynamically adjust them to more optimally achieve stated goals.

Committing to such a transition implies that we can determine which pollutants or mixtures sensitive sub-populations are being exposed to, and that we can determine the relative risks associated with these exposures. Further, such a transition requires that objective procedures be designed to assess these risks, identify appropriate actions for reducing them, and measure the effectiveness of these risk-reduction actions.

4.1 Risk Assessment and Its Components

The concept of risk analysis has been applied in a variety of programs for protection of human health and welfare. The formalism of risk analysis has been discussed in a number of monographs and reports, such as NRC (1983), and is further detailed in Appendix A (http://www.narsto.org/).

Risk analysis involves development of decision alternatives for reducing or managing risk, valuation of the alternatives, decision making to choose an alternative, implementation of the decision, evaluation of the effectiveness of the decision (also labeled “accountability”) and iteration on the decision over time. The last two steps, accountability and iteration, are an inherent part of the proposed multipollutant framework put forward in Fig. 3.1.

4.1.1 Risk Assessment

The starting point for the logic of Fig. 3.1 is human activity, the source of air pollution. Human activities include many functions such as the extraction of raw materials, conversion of these materials to goods and services, and use of these goods and services (e.g., electrification, heating, cooling, and transportation) by consumers. Human activity is influenced by factors such as age, gender, socio-economic status, and disease status. It can also be influenced at high temporal and spatial resolution by weather (i.e., rain, snow, and storms can lead to short-term changes in transportation and other energy use).

Human activities emit gases and particles to the atmosphere where they may become pollutants or alter the environment in some way (as through anthropogenic climate change). Once in the atmosphere, these “primary” emissions combine with emissions from natural sources and become subject to physical transport (horizontal or vertical advection), physicochemical transformations, and removal. Chemical transformation can result in the production of new gas or particulate pollutants (called secondary pollutants), and can lead to changes in the chemical composition of atmospheric particles.

When primary and secondary pollutants come in contact with humans, ecosystems, or other receptors, an exposure occurs. Dose differs from exposure. Dose is what is delivered to an affected organ or ecosystem component. Exposure is sometimes referred to as potential dose because it is an upper bound on the actual (but often unknown and hard to quantify) internal dose. Once a dose occurs, the receptor organ or system reacts in ways that if the dose is high enough or prolonged enough could, in the case of humans, range from symptoms such as acute respiratory distress to chronic illness including cancer. The portion of risk assessment that is concerned with quantifying the frequency and severity of exposure and dose outcomes is risk characterization.

When analysts conduct a risk assessment, substantial differences in the quality and quantity of information available for individual components of the analysis quickly become apparent. Initially it may only be possible to quantify the first few components of the source-to-outcome continuum. For example, in the absence of exposure-response data for a particular pollutant, or regarding interactions among multiple pollutants, either simplifying assumptions are made or the exposure-response portion of the analysis is omitted. If the latter, then decision making may be based on a surrogate measure of risk, such as community level exposure or ambient concentration, rather than on a direct estimate of risk. Such surrogates can be useful as interim information until a more complete characterization of risk is possible, but there is also the possibility that a surrogate could be misleading with regard to the actual effect of management options on risk.

Risk characterization can include (but not be limited to) one or more of the following: (a) risk to human individuals (e.g., lifetime individual risk of cancer); (b) risk to human populations (e.g., expected number of premature deaths due to excess cancers attributable to air pollution exposure or dose); and (c) ecological impacts—usually focused on populations rather than individuals (e.g., survival of a plant, insect, or animal species). Risk characterization also provides information on the timing of the risk and information on uncertainty and variability generated through the risk analysis. It also provides a context for characterizing and communicating the magnitude and breadth of the risk, for example, by relating it to other more familiar human activities (e.g., a one in a million risk of death is about half the risk of dying in a train accident). However, these types of risk comparisons must be made with care. Risks differ not only in their magnitude, but also in other attributes, such as whether the risk is voluntary or involuntary, how dreaded the risk is (e.g., cancer versus sudden death from a car accident), and the temporal latency of the risk. Hence, risk communication must be done with care so not to inappropriately co-mingle these attributes that affect risk perception.

4.1.2 Risk Management: Valuation and Decision Making

The discussion above characterizes risk assessment, which is a science-based process. Risk management involves using the results of a risk assessment in the decision-making process. A risk assessment should be developed to answer questions of relevance to stakeholders and decision makers, as detailed in Appendix A. One potential aspect of the risk management decision process is to place a value on the adverse effects associated with the risk or, conversely, on the damages that could be avoided by reducing the risk. Therefore, once risks have been identified and, in some cases, quantified, a valuation process can proceed. This part of the process depends on societal values. Thus, while it can be framed as part of a formal decision methodology, risk management is inherently subjective and based on policy considerations.

The valuation process deals, either explicitly or implicitly, with the relative value placed on avoiding adverse effects identified during risk characterization (e.g., should there be more focus on preventing excess cancers in humans or on avoiding damage to ecosystems, if there are such trade-offs), and also the amount of resources that should be devoted to risk management. However, these issues are separate, at least conceptually, from the scientific assessment aspects of dealing with the emission-to-risk characterization aspects of a risk assessment. For several perspectives on the valuation of risk reductions, see discussions by Bateman et al. (2002); Hofstetter and Hammitt (2002); and Miller et al. (2007).

Risk management options are policy choices on how to modify emissions or human activity to change downstream exposure, dose, and risks. Such options could focus on technology-based solutions (e.g., end-of-pipe emission control technologies, or substitution of feedstocks,) or on changing demand for goods and services in the economy. The latter can include production processes (e.g., energy efficiency improvements) and consumer demands (e.g., purchase of hybrid vehicles) to reduce pollution emissions.

Iteration is an important follow-on to the initial risk management and decision-making process. Periodic evaluation of the effectiveness of management options once selected and implemented is an inherent part of the combined risk assessment and risk analysis process.

4.1.3 Integrating Components of Risk Assessment and Risk Analysis

Most of the current focus of multipollutant management and analysis has been on emissions and air quality components. To date (at *Levels 1* and *2* as set forth in Chap. 3), little has been done on characterizing multipollutant exposures, doses, and outcomes, for example, as described in Chaps. 5 and 6. As such, multipollutant management has been limited to prescribing control options that reduce multiple pollutants, without regard to the potential interactions between or relative magnitudes of exposures and risks associated with different combinations of pollutants. In part this reflects the institutional and legal frameworks, summarized in Chap. 3, within which management decisions are made. In the United States, for example, the structure of the Clean Air Act leads to the setting of separate standards for individual pollutants (e.g., NAAQS) or for individual source categories (e.g., New

Source Performance Standards, National Emission Standards for Hazardous Air Pollutants, mobile source emissions), which restrict how multi-source and multi-pollutant risks might be incorporated into management strategies. Similar policy constraints exist in Canada and Mexico.

4.2 Accountability

The risk-based framework is a structure that can be used both for integrated assessment of multi-pollutant air quality management actions and for accountability, as illustrated in Fig. 3.2. The components of this framework that apply to accountability assessments include measurement of the effect of implemented risk management strategies on changes in emissions, pollutant transport and fate (air quality), exposure, dose, and effects (risk characterization). These components can be simplified in some cases. For example, exposure and effects could be combined into an exposure-response component that also includes risk characterization. For each component, data and modeling tools can support integrated assessments at correspondingly varying degrees of confidence. For example, for determining emissions, there are direct measurements of some pollutants from some sources, and surrogate or proxy measurements of other source/pollutant combinations. Measurements should be relevant to the averaging times of interest for the integrated accountability assessment. For other cases in which emission data may be unavailable, emissions are estimated using mass balance or other methods (NARSTO 2005). Current methods used for developing emission inventories would be a starting point for conducting a multipollutant, integrated assessment.

While integrated assessments support the design and execution of air quality management actions, accountability is a process for verifying whether predicted reductions in emissions, air quality, exposure, dose, and/or risk were actually achieved. If not, the accountability process entails determining why not and what can be done to correct the air quality management actions or to improve the prediction/estimation process. To determine whether ambient exposure actually decreases as a result of an emission control strategy or regulation, one could begin with continuous emission monitoring (CEM) or conduct emission source tests before and after the change to verify the actual change in emissions. In order to do this in a manner that is useful with respect to human or environmental health objectives, one would verify corresponding changes in ambient conditions at temporal and spatial scales relevant to the risk-based, adverse effect endpoints.

A key consideration in conducting a prospective analysis to predict and manage risk reduction, as well as to conduct a retrospective accountability assessment, is to use a parallel structure, as illustrated in Fig. 3.2. The prospective analysis, whether it is referred to as risk analysis, integrated assessment, or by some other name, is intended to predict the results of management actions, usually incorporating reductions in emissions, ambient concentrations, exposure, and risk. Such an assessment is done to support decision-making processes. The accountability assessment is conducted after actions have been taken to determine whether they actually accomplished the predicted reductions. The outcome of an accountability assessment can feed into a new or updated risk or integrated assessment or directly support decision making on whether to modify the risk management strategy. *In order for both the predictive and retrospective approaches to be most meaningful, they should be based on common metrics and take into account similar framings of the problem.* For example, the spatial and temporal resolution of modeling and monitoring needs for emissions, air quality, exposure, and risk should be commensurate and based on the health and environmental outcomes of concern. If the predictive and retrospective approaches do not match with respect to spatial and temporal resolution and key metrics, then the ability to make causal inferences regarding accountability is compromised.

4.3 Risk Assessment in Current Regulatory Practice

Risk assessments are conducted for a number of purposes within Canada, Mexico, and the United States. In the three nations, risk analyses have been used to help inform the setting of ambient air quality standards for public health and ecosystem protection, to evaluate risks from exposure to air toxics, and as inputs to cost-benefit analyses. While risk assessments for human health effects are relatively common, assessments of ecological risks from air pollution are less so, and are generally more limited in scope and execution. This relative lack of ecological risk assessments reflects the additional analytical elements that are required to conduct them, the much greater heterogeneity in the susceptibility of receptors, and the diversity of receptors (see also Chap. 6).

In recent years, assessments of ecosystem risk changes have been conducted by EPA for the Clean Air Interstate Rule (which has recently been vacated and subsequently reinstated by U.S. federal courts), focusing on the change in risk of acidification related effects in freshwater rivers and lakes. In addition, limited assessments of the impacts of ozone on commercial forest productivity and agricultural productivity have been conducted; however, these analyses have only focused on quantifying the direct commercial impacts of changes in forest and crop yields, and have not looked at overall sets of ecosystem services (e.g., SAB 2007).

For the current review of the secondary NAAQS for NO_x and SO_x, EPA has completed a more ambitious risk assessment accounting for the interactions between the two pollutants in determining ecosystem risks associated with acidification and nutrient enrichment (EPA 2009). This analysis marks the first time EPA analyzed the joint ecosystem risks of two criteria air pollutants, and provides an opportunity to improve ecosystem risk assessment methods and provides a greater understanding of the challenges that remain.

Examples of analyses of human risks to exposure from air pollution are summarized in Sect. 4.3.1 in the context of population risk for criteria air pollutants, representing case study examples from Canada, Mexico, and the United States. Section 4.3.2 presents an example of risk analysis for hazardous air pollutants. These case studies pertain mostly to CPs, for which risk assessment approaches typically focus on population risk measures, particularly for susceptible subpopulations. For HAPs, the risk assessment approach typically focuses on individual and population risk, as described in the case study example. This approach is applied exclusively in the United States at the present time, in keeping with the CAA requirements.

4.3.1 Examples of Risk Assessment for Criteria Pollutants

4.3.1.1 Evolution and Application of Integrated Risk Models in Canada

Evaluation of options for improving air quality requires information on the projected benefits to human health and the environment arising from each option. Predictive models for this purpose have been an important component of air quality management in Canada for over 10 years. The NARSTO PM Assessment presented an example of how air quality changes were determined for changes in gasoline and diesel sulfur content for subsequent application in risk and economic models (Brook et al. 2004). A multipollutant extension of that work (Burnett et al. 1998), to not only account for the risks/benefits arising from $PM_{2.5}$ (sulfate) change but also arising from decreases in gaseous pollutants (e.g., NO_x and CO emission reduction expected from improved catalysts), ultimately had a significant impact on the air quality management processes. Since this Canadian 'Sulfur-in-Fuel' exercise, the integrated risk models have continually evolved to address limitations that effort served to highlight.

Future regulations are currently being considered for Canadian industrial sectors, and several model applications have been undertaken to consider various scenarios. This was done in multiple steps (see Appendix A, www.narsto.org) by combining models for changes in emission inventories with changes in air concentration and deposition predicted by AURAMS (Chap. 9 and Appendix A). These results were then used to infer changes in impacts and in economic benefits. In one scenario focusing on 16 industrial sectors, such as electricity generation, cement production, refineries, steel and upstream oil and gas activities, Canadian SO_x, NO_x, VOC and $PM_{2.5}$ emissions from anthropogenic sources were estimated to decrease by 50, 23, 20 and 6%, respectively, compared to the 2015 projected emissions. Alberta and Northern British Columbia would have the greatest reductions for this scenario, while in the rest of Canada small reductions are spread over most of the populated areas.

Changes in ozone predicted in this analysis are shown in Fig. 4.1. These changes are widespread for summertime levels, ranging from 1 to 3 ppb (i.e., 5–10%) in the Prairies and Northern Ontario. They are 5 ppb or higher in Alberta and Northern Saskatchewan, while in the more populated areas such as Vancouver, the Windsor-Quebec City corridor and the southern Atlantic coast, the predicted improvements rarely exceed 3 ppb or <5%. Changes in $PM_{2.5}$ are shown in Fig. 4.2. These exceed 1 $\mu g/m^3$ or 10% in central Alberta, and the magnitude of the improvements in the

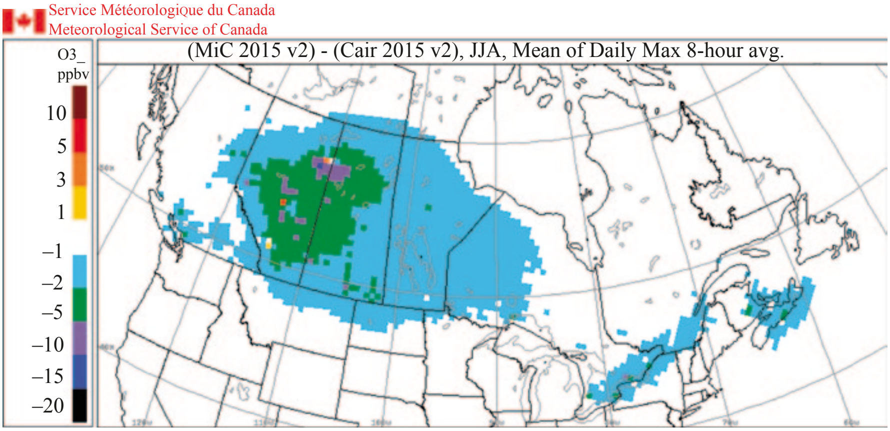

Fig. 4.1 Calculated change in average summertime daily 8 hr maximum ozone (ppb)

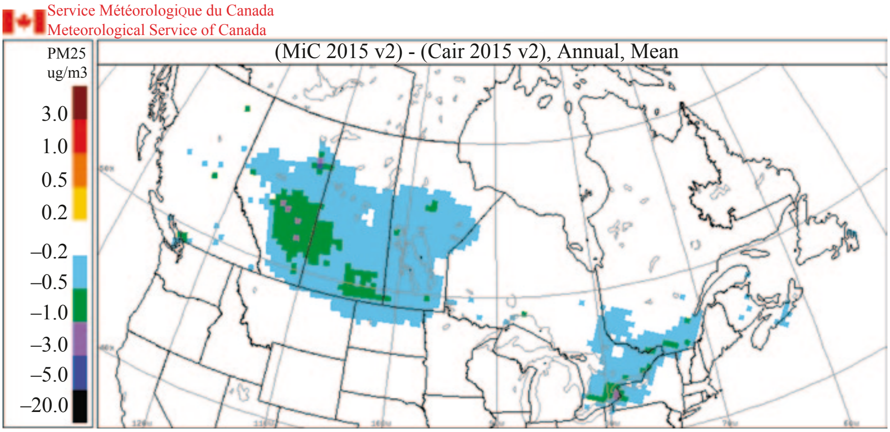

Fig. 4.2 Calculated change in annual $PM_{2.5}$ concentration ($\mu g/m^3$)

Windsor-Quebec City corridor is larger than the ozone change, ranging from 0.2 to 1 $\mu g/m^3$ or 5–10%). The Maritimes (i.e., Atlantic Coast) and the Vancouver area only experience marginal improvements on an annual basis for this scenario. Overall, the changes predicted by the analysis lead to reductions in population weighted ambient exposures to summertime ozone of about 3%, and year round $PM_{2.5}$ of about 8%.

The health benefits associated with the projected improvements in exposure are summarized in Table 4.1. $PM_{2.5}$ changes account for the greatest share of the benefits. This is because of the greater estimated effects on human health of long-term exposure to $PM_{2.5}$ relative to ozone, based upon the information currently available to the AQBAT model (see Appendix A, www.narsto.org). The total health benefits estimated by AQBAT are generally believed to be underestimates because they are not based upon all or multiple pollutants; only ozone and $PM_{2.5}$ exposure are con-

Table 4.1 Estimated reduced numbers of health impacts based upon the scenario compared to the BAU 2015 base case. (mean and 95% upper and lower confidence intervals)

Health outcome	Mean	Lower	Upper
Premature deaths	1,200	740	1,700
Chronic bronchitis cases	920	–	1,800
Hospital admissions	260	160	360
Emergency visits	1,000	540	1,500
Child acute bronchitis episodes	5,600	–	12,000
Asthma days	170,000	67,000	270,000
Restricted activity days	1,000,000	600,000	1,400,000
Minor restricted activity days	210,000	–	910,000
Minor symptom days	3,400,000	870,000	6,000,000

sidered. Furthermore, only some health outcomes can be quantified because of a lack of information. Nonetheless, the total annual social welfare benefits in the year 2015 from the reduced risk of death and illness shown in Table 4.1 are estimated to be worth \$6.4 billion.

In terms of environmental benefits, the reduced ozone levels shown in Fig. 4.1 and subsequent reductions in the associated stress to agricultural plants are estimated to result in an increase in production for key agricultural crops; valued at \$123 million in Canada. It is likely that the total benefits to agriculture are higher, because the crops modeled only account for roughly 60% of the value of all crops and the impacts of soil acidification are not included. The improvements in visibility stemming from the predicted $PM_{2.5}$ change in Fig. 4.2 are estimated to be worth \$144 million to Canadian residents. Considerable challenges remain in estimating costs of environmental damage. Although evaluation techniques for estimating environmental damage have improved, there is still a significant gap in the research needed to develop more comprehensive valuation models.

4.3.1.2 Risk Assessment in Mexico

Researchers in Mexico have conducted several recent evaluations of the potential health impacts associated with PM and ozone in Mexico. These analyses have used both Mexican and U.S. epidemiological studies to inform health impact functions that are applied to Mexican emission and air quality data. In Mexico, differences in the health risks associated with acute and chronic exposures to pollutants are not as well characterized as in the United States. Although air quality standards for both types of exposures exist, populations are generally more informed about acute exposures and are less familiar with the risks associated with chronic exposures. As a result, Mexican researchers have begun developing risk assessments to inform decision makers of the potential benefits of reducing long-term exposures to air pollution.

Mexican risk assessments have also examined the impacts of known carcinogens on risk of cancer. In Mexico City, urban populations are exposed to both criteria pollutants and air toxics (Evans et al. 2002; Shiohara et al. 2005; Carmona-Villavicencio 2006). Ambient concentrations of formaldehyde range from 8 to 45 µg/m^3 (Shiohara et al. 2005) compared with the EPA's Office of Environmental Health Hazard Assessment reference level of 3 µg/m^3. Monthly average benzene concentrations are about 10 µg/m^3 (Grutter and Flores 2004). This level hypothetically could induce around 61 cancer cases per million people exposed.

For non-cancer effects of criteria pollutants, Mexican risk assessments have used a damage function approach similar to that used in the United States and Canada. However, the concept of hazard coefficients is also used. In this method, a hazard coefficient value above one indicates that the exposure of a person is above the recommended level of exposure. In Mexico, non-cancer risk assessments have been applied to estimate hazard coefficients for exposures of adults and children in Monterrey (Mejía and Zavala 2003) and Ciudad Juárez (Mejía et al. 2004) and for the general population in Mexico City (Garcia et al. 2007).

To complete a damage function based analysis of the benefits of air pollution risk reductions, several parameters need to be estimated for Mexico (Evans et al. 2002). These include dose-response coefficients, exposure patterns of Mexican populations, and actual medical expenses for treatment of asthma, chronic bronchitis, allergies, and other health outcomes. Other inputs for estimating economic benefits include estimates of the willingness to pay to reduce risk mortality and morbidity (Hammitt and Ibarraran 2006).

In the case of ozone, EPA's BenMAP model was used along with local observed ambient ozone concentrations to evaluate benefits for reductions of ambient ozone concentrations in Mexico City (Reyes-Cortes and Lorena 2006).

Using a damage function approach, Galindo and Caballero (2007) have estimated that increases in emissions of PM_{10} in the Valley of Mexico (including Mexico City) through 2025 will result in over 52,000 premature deaths due to long term exposure to PM_{10} and close to 120,000 cases of chronic bronchitis, while reductions in ozone precursor emissions will decrease ozone related premature deaths by over 12,000.

Two risk assessment studies have been developed for the Monterrey Metropolitan Area (MMA). One study was related to exposure to ozone and PM_{10}. The other study was a benefit analysis of PM_{10} reduction. A PM_{10} risk assessment study also was developed for the Ciudad Juárez/El Paso Area. Additional description of these assessments is provided in Appendix A.

4.3.1.3 Risk and Benefit Analysis of U.S. Regulatory Programs

EPA recently has issued a number of regulations for stationary and mobile sources that are expected to substantially reduce ozone and PM_x ($PM_{2.5}$–$PM_{10\text{-}2.5}$) precursor emissions. One significant example is the Clean Air Non-road Diesel Rule (CANDR). EPA conducted risk and benefit analyses in support of these regulations. The CANDR analysis suggests that when the nonroad diesel engine emission reductions are fully realized in 2030, they will result in substantial, broad scale reductions in

$PM_{2.5}$ (population weighted reduction of over 0.5 μg/m^3). This change is associated with an estimated 2030 annual reduction in the incidence of premature mortality by 9,600, chronic bronchitis by 5,700, nonfatal myocardial infarctions by 16,000, and respiratory and cardiovascular hospital and emergency room admissions by 14,000. In addition, over 200,000 asthma exacerbations and millions of respiratory symptoms are predicted to be avoided in 2030. An economic value of these health benefits is estimated at over $90 billion (also, see Appendix A). Monetized benefit estimates are sensitive to choice of the concentration-response function for premature mortality, valuation of mortality risk reductions, assumed lag/latency structure, and assumptions about the shape of the concentration-health response function. However, under the Agency's assumptions, health risk reductions from this rule are calculated to be substantial.

EPA also has conducted a set of risk analyses to support the NAAQS decision making, as well as benefit-cost analyses as part of the regulatory requirements under Presidential Executive Order 12866. The benefit-cost analysis includes an overall assessment of health and welfare impacts of achieving the standards. A specific example is the recent $PM_{2.5}$ analysis given in Appendix A. As interpreted by the Agency and the courts, the CAA prohibits EPA from considering costs in *setting or revising* any national air quality standard.

There are some important differences in the scope and methods used in NAAQS risk analyses versus benefits analyses. Table 4.2 lays out some of the key differences. The primary differences reflect the purposes of each analysis. The NAAQS risk assessments are intended to provide quantitative estimates of the risk to public health associated with existing (single pollutant) air quality levels and with air quality levels that would occur if current and alternative standards are achieved. Such information is intended to assist the EPA Administrator in selecting primary standards that will protect the public health with an "adequate" margin of safety, recognizing that such standards will not be risk-free. In these types of assessments, a premium is

Table 4.2 Comparison of U.S. EPA NAAQS risk analyses and its benefits analyses

EPA NAAQS risk analysis	EPA NAAQS benefits analysis
Location-specific, matched with studies	National extrapolation of study results
More refined baseline incidence rates	National or regional baseline incidence rates
Focus is often on sensitive subpopulations	Focus on expected outcomes in the general population
Detailed exposure modeling for health endpoints based on controlled human exposure studies, otherwise uses ambient concentrations	Uses only ambient concentrations
Uses monitored air quality data for current or recent years	Uses modeled and monitored air quality data
Does not project to specific future years, but adjusts air quality data to simulate just meeting current and alternative standards	Often uses projections to future years
Generally fewer health endpoints	Comprehensive set of health and welfare (e.g., visibility) endpoints

placed on reducing the level of uncertainty in the quantitative estimates. In the case of benefit analyses, the purpose is to develop a comprehensive assessment of health and welfare impacts (including multiple pollutants) of illustrative strategies to attain alternative standards, which can be assigned economic values for comparison with costs of the strategies. In these benefit analyses, a balance between comprehensiveness and precision is sought, because of the direct comparison with costs.

Through the different types of risk analyses, EPA management has been informed about the significance and consequences of improvement in environmental protection afforded by revision of the standards, or implementation of new regulations. The added insight from the risk analyses is believed to have improved substantially the $PM_{2.5}$ air quality management practices in the United States.

4.3.2 Risk Assessment for Hazardous Air Pollutants

In addition to risk analyses for CPs, which are illustrated in Appendix A, EPA conducts risk assessments to support regulations controlling sources of air toxics or HAPs. These risk assessments are focused on a different risk management objective than those for CPs. The purpose of these risk assessments is to assess health risks from exposure to routine emissions of all air toxic pollutants from all sources in a category (e.g., petroleum refineries, chemical processing, and steel mills) to inform regulation. These assessments are intended to estimate the health and environmental risks remaining after implementation of Maximum Achievable Control Technology (MACT) standards. EPA then establishes emission standards to address remaining or residual risks.

EPA's approach for residual risk assessment is to calculate the risks associated with emissions of HAPs from large groups of sources. These risk assessments use current emission data from potential sources of risk, after sources have met applicable MACT standards. The assessment is focused on those HAP emissions expected to have the most impact on human health risk; e.g., those with the highest relative cancer potency- and chronic non-cancer hazard-weighted emissions for each source category.

The goal of the risk assessment is to estimate acute and chronic cancer and non-cancer risks, the distribution of risks across affected populations and cancer incidence. The HAP risk analyses focus on two types of human health risk metrics: the Maximum Individual Risk (MIR), and total population cancer incidence attributable to the source category.

HAP risk analyses use the Human Exposure Model in combination with the American Meteorological Society/EPA Regulatory Model dispersion modeling system (HEM-AERMOD). HEM-AERMOD performs three main operations: dispersion modeling, estimation of individual human health risks, and estimation of population risk.

Dose-response assessment information for chronic exposures is based on the EPA Office of Air Quality Planning and Standards' existing recommendations for

HAPs. EPA's assessments typically specify a reference concentration (RfC) to protect against effects other than cancer and/or a unit risk estimate (URE) to estimate the probability of developing cancer.

The multi-media, multi-pathway screening analysis of indirect human health and ecological effects is carried out using a screening level version of the Total Risk Integrated Methodology (TRIM), a state-of-the-art modeling platform for assessing the fate and transport of air pollutants that can deposit from the atmosphere and transport through soil, water, and biota before they are ingested (see http://www.epa.gov/ttn/atw/urban/trim/trimpg.html).

EPA synthesizes the results of the HAP risk assessments in a risk characterization, in which information from the individual steps in the risk analysis is integrated and an overall conclusion about risk is synthesized that is complete, informative, and useful for decision makers. In general, the nature of a risk characterization depends on the information available, the application of the risk information and the resources available. This risk characterization addresses or provides descriptions of risk from each of the source categories assessed to: (a) individuals exposed to both the central and high-end portions of the exposure distribution; (b) the exposed population as a whole; and (c) important subgroups of the population such as highly exposed or physiologically susceptible demographic groups or life stages, if known.

EPA recently completed a risk assessment for HAP emissions from petroleum refineries (EPA 2007). Table 4.3 summarizes the results of the risk analysis, demonstrating the different types of risk metrics developed for HAP regulations. The results summarized in the table suggest that over 10% of the petroleum refineries analyzed had maximum individual risks over ten in one million, and over 60% had MIR over one in one million. However, the total annual excess cancer incidence over the entire U.S. population is estimated to be well under one case per year. This reflects the highly skewed nature of the exposure distribution for proximity to these facilities, and demonstrates well the difference between individual and population level risks.

4.4 Combining or Comparing Risks Across Pollutants

While it is relatively straightforward to compare human health impacts across CP goals or standards, it is not an easy task to compare health risks between CPs and HAPs, or to compare overall human health and ecosystem risks. Furthermore, there is a need to combine the assessment of exposure and risk associated with multiple pollutants, which requires consistent metrics. While it is possible to compare the incidence of health effects between existing analyses of CPs and HAPs, the interpretation is not straightforward because the objectives of these analyses differ with respect to risk endpoints and policy goals. For many HAPs, the relative risks may seem small in magnitude compared to those addressed by national-scale regulations on CPs such as $PM_{2.5}$, or precursors such as VOCs. However, the purpose of the HAPs regulations is not only to reduce population level impacts, but to reduce

Table 4.3 Summary of hazardous air pollutant risk analysis results for petroleum refineries. (Source: Draft residual risk assessment for MACT I petroleum refining, EPA 2007)

Result		HAP "Drivers"
Facilities in source category		
Number of facilities identified in NEI and modeled in screening risk assessment	153	n/a
Cancer risks		
Maximum individual lifetime cancer risk (in 1 million) from any facility in the category	70	Ethylene dibromide
Number of facilities with maximum individual lifetime cancer risk:		
Greater than or equal to 100 in 1 million	0	n/a
Greater than or equal to 10 in 1 million	21	Ethylene dibromide, POM, benzene, naphthalene, 1,3-butadiene, chromium (VI), arsenic, beryllium, cadmium, tetrachloroethene
Greater than or equal to 1 in 1 million	96	Ethylene dibromide, POM, benzene, naphthalene, 1,3-butadiene, chromium (VI), arsenic, beryllium, cadmium, tetrachloroethene, carbon tetrachloride, methyl tert-butyl ether, ethylene dichloride, lead
Chronic noncancer risks		
Maximum respiratory hazard index	0.3	Diethanolamine (CalEPA REL)
Number of facilities with maximum respiratory hazard index:		
Greater than 1	0	n/a
Acute noncancer screening results		
Maximum acute hazard quotient	130	Acrolein (REL)
Number of facilities with potential for acute effects	25	Arsenic, acrolein, benzene, formaldehyde, glycol ethers, hydrofluoric acid, methanol
Acute noncancer refined results		
Maximum acute hazard quotient	70	Acrolein (REL)
Number of facilities with potential for acute effects	14	Acrolein, arsenic, benzene, formaldehyde, hydrofluoric acid
Population exposure		
Number of people living within 50 km of facilities modeled	90,000,000	n/a
Number of people exposed to cancer risk:		
Greater than or equal to 100 in 1 million	0	n/a
Greater than or equal to 10 in 1 million	6,000	n/a
Greater than or equal to 1 in 1 million	460,000	n/a
Number of people exposed to noncancer respiratory hazard index:		
Greater than 1	0	n/a
Estimated cancer incidence (excess cancer cases per year)	0.05	n/a

maximum individual risks as well, and these reductions are not easily compared with NAAQS programs. These are intended to reduce broad public health impacts. In a multipollutant framework addressing management *Levels 3* and *4*, consistent goals and metrics are needed.

4.5 How Is Risk Information Used in the Decision-Making Process?

While the basic framework for risk assessment is consistent across applications, the specific scope and elements of risk assessment often vary based on their purpose. In the case of NAAQS risk assessment, the results from an assessment may be used as information to support the decision made by the EPA Administrator in setting the standard. In the case of the benefit analysis for a regulation such as the U.S. Non-road Diesel Rule, the risk analysis may be used as part of a larger benefit-cost analysis which can help to inform the level of stringency of fuel and engine standards. For the NAAQS, benefit-cost analysis is not part of the process of setting the regulation, since under the Clean Air Act costs may not be considered when determining NAAQS levels for each CP. In some cases, such as regulations focused on air toxics (HAPs), the objectives of the regulation may not be solely to improve overall public health, but instead to address disproportionate risk in a segment of the population. In these cases, equity rather than efficiency may be a guiding objective, and thus a particular rulemaking may not be guided or constrained by benefit-cost analysis. Risk and benefit analyses can also be useful for a variety of other activities including public interactions on proposed regulations and informing the design of legislative proposals.

4.6 Assessment with Multipollutant Air Quality Management

To date, most *Level 1* and *2* assessments of risks and benefits have focused on either a single pollutant, as in the case of NAAQS risk analyses, or a set of pollutants controlled by a regulation focused on one or several pollutants, as in the case of the benefits analyses of CAIR and the Non-road Diesel Rule. In general, these analyses have not focused on identifying the set of pollutants or their levels that would optimally reduce overall risk from exposure to atmospheric pollution.

To develop a risk-based air quality management process, a clear understanding of the definition of risk needs to be established. For example, risk can be defined in terms of individual risk (e.g., individual risk of cancer) or population risk (e.g., overall population risk of death from pollution-related causes). In addition, a framework for combining and comparing risks across different pollutants is necessary to move toward *Levels 3* and *4*. The knowledge, in extent and quality, from emissions to effects varies greatly by pollutant or groups of pollutants. Criteria pollutants as a group are better characterized for risk assessment than HAPs. In all cases, the dose-response or concentration-response functions vary in quality and in format, depending on the endpoints of human health effects. At one extreme, many of these functions for HAPs are based solely on laboratory animal studies, while at the other extreme CPs (such as SO_2 and NO_x) have extensive investigations from the laboratory combined with epidemiological results from multiple cities. Incorporating these widely different exposure-effects estimates into a uniform risk model represents a significant challenge for the analyst.

An important policy question is whether or not human health risks and risks to ecosystem functions can be combined in a single air quality management optimization framework. Because of differences in the types, locations, or spatial and temporal scales of ecological vs. public health risks, it may be impractical to develop a fully integrated framework. Without integration, however, conducting separate optimization exercises may lead to contradictory or suboptimal air quality management plans.

4.7 Risk Communication

An important component of the risk management process is risk communication, both between analysts and decision makers and between analysts and stakeholders. The process of risk communication often requires the steps of translation, simplification, and condensation. The step of translation requires the analyst to often take complex scientific outputs and translate them into metrics that have meaning to decision makers and stakeholders. An example is the translation of spatially distributed, speciated particulate matter concentrations into population exposure beyond specified levels of PM standards. The step of simplification requires the analyst to take very complex integrated analyses, which often require dozens to hundreds of steps, and simplify these to a few key analytical elements. The step of condensation requires the analyst to: (a) summarize the results of a risk analysis, usually taking detailed results in space and time and condensing them into a uniform interpretation; (b) find ways to communicate the sensitivity of results to different modeling assumptions; and (c) characterize the qualitative and quantitative uncertainty in results.

EPA has developed a number of graphical approaches for summarizing and displaying risk estimates and their associated quantified uncertainty. For example, Fig. 4.3 reproduces a graphic from EPA's risk assessment for the 2006 PM NAAQS review. In that risk analysis, the uncertainty analysis included only the statistical uncertainty surrounding the estimates of the concentration-response functions. In Fig. 4.3, one can readily see from the confidence intervals the variation from study to study in the mortality estimates. Nevertheless, the reader also can see that all the estimates reported in the figure show an increase in mortality risk with $PM_{2.5}$ exposure.

Summarizing risk analysis results in a multipollutant risk framework is even more challenging, and may require development of additional methods. One could envision two-way probability plots showing the bivariate distribution of benefits

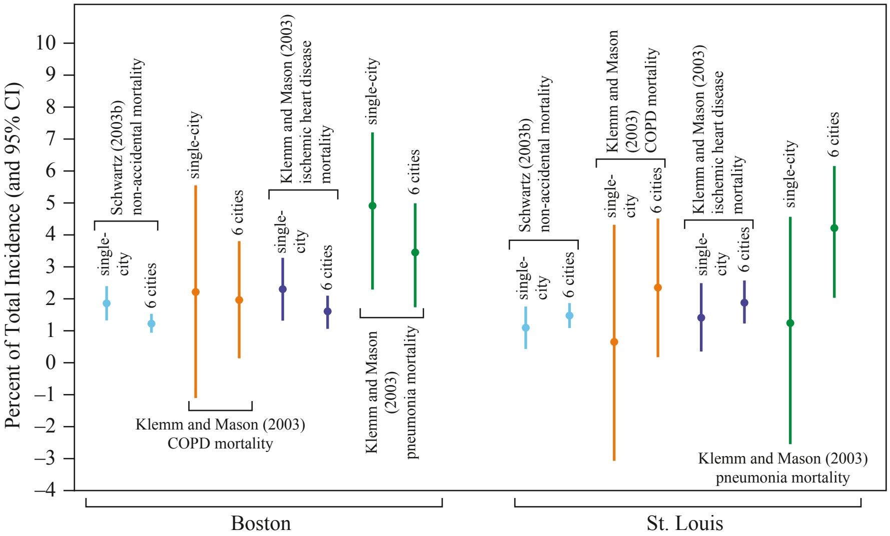

Fig. 4.3 Estimated annual percent of total (non-accidental) mortality associated with short-term exposure to $PM_{2.5}$ above background (95% confidence intervals are indicated by the extent of vertical lines through the mean value): single-city versus multi-city models. (From Fig. 5.4, EPA 2005)

across two pollutants, but with greater than two pollutants, graphical displays become less useful.

Risk communication also involves communication of the strengths and weaknesses of the analytical techniques used to generate estimates of risks. Decision makers need confidence in the analytical techniques to accept them as credible for inclusion in the decision-making process. Especially in the case of complex integrated risk models, decision makers may want to understand the justification for model inputs and parameters, as well as understand model outputs, uncertainties, and their implications for management policies.

Because modeling for risk analysis requires combining actual data with assumptions, improved communication with decision makers and stakeholders to explain or interpret adopted assumptions is necessary. Additional sensitivity analyses may also be required to show the implications of choosing realistic alternative assumptions. Such complexities will be found in applying principles of risk analysis to multipollutant air quality management decisions in the future.

4.8 Limitations of Multipollutant Risk Analysis for Regulatory Applications

The greatest challenges in multipollutant risk assessment are the current limited information supporting risk characterization through concentration-response or dose-response information that includes exposure. As discussed in Chap. 5, dose (or concentration)-response assessment and risk characterization is typically considered for a specific, individual pollutant. In many cases, there are multiple health effect endpoints for a given pollutant, as well as disparate, parallel health effects associated with each of many pollutants. There are challenges to the assessment of interactions among multiple pollutants (e.g., synergisms, or antagonisms) with respect to dose and response, and thus there are many uncertainties and knowledge gaps that need to be filled in order to refine these aspects of the risk assessment. As noted earlier, even if a "perfect" dose and risk characterization can be performed, there are challenges regarding how decisions should be made by taking into account the multipollutant nature of sources and chemistry, given the nature of exposure to populations and the potential for adverse health effects from exposure to multiple pollutants at varying ambient concentrations.

In spite of these challenges, there are distinct advantages to conducting risk assessments in a multipollutant framework. One such advantage is the ability to use a single comprehensive calculation to characterize risks for multiple pollutants of interest. Given the costly nature of detailed photochemical modeling and exposure modeling, this advantage can reduce the overall costs of risk analyses, and allow for more sensitivity calculations, or an evaluation of a broadened number of policy scenarios.

Another advantage of a multipollutant approach is the avoidance of an "ordering effect," where the incremental risk changes resulting from single pollutant policies are dependent on the order or sequence in which they are assessed. For example, in EPA's recent benefit-cost analyses of the PM and ozone NAAQS, attainment of the PM NAAQS was analyzed first, and resulted in substantial estimated net benefits for both pollutants. In that analysis, significant levels of NO_x emission reductions were applied in portions of the western United States to reduce nitrate concentrations that contribute to nonattainment of the annual and daily PM standards. In a subsequent analysis of the proposed ozone NAAQS, the proposed NO_x emission reductions were included in the baseline for the analysis, and more extensive VOC and NO_x reductions were then applied to attain the ozone standard incremental to attainment of the PM standards. The results of the ozone analysis showed a range of net impacts including both net costs and net benefits, which were substantially below the net benefits for the PM standard alone (EPA 2006, 2008). The results would likely have been different had the ozone standard been analyzed first. More importantly, had the two standards been analyzed together, incremental to a baseline with attainment of the previous set of PM and ozone standards, the results could have created an "optimized" management strategy.

4.9 Summary

Risk assessment is a useful multipollutant framework for integrating and evaluating diverse sets of data and models to produce metrics to aid in decision making. The ability to implement a risk assessment framework in a credible and policy-relevant manner depends on the availability of component models and data that are scientifically sound and are developed with an understanding of their application in integrated assessments. The same can be said about accountability assessments used to evaluate the outcomes of decisions made using such frameworks:

- Current approaches and experience with single pollutant risk assessments show the utility of this information in decision making. Formal risk analyses are used in support of the setting of national standards in North America, recognizing uncertainties and limitations in the available analytical data and methods. Results from these analyses point to the targets, goals and metrics that can similarly be applied to evaluate the outcomes under an accountability framework.
- Key strengths of single pollutant risk assessments include the use of well-defined health endpoints, "weight-of-evidence" approaches to determine the likelihood of causal relationships and exposure, well characterized monitoring and modeling data for air quality, and careful reporting of quantified and unquantified uncertainties.
- Key limitations of air pollution risk assessments include incomplete knowledge of population exposure and health effects, inability to completely control for co-pollutant confounding and effect modification, and the lack of individual exposure-based health-response functions.

Some of the important uncertainties and gaps in knowledge regarding risks associated with multipollutant exposures, which have yet to be resolved, are:

- Uncertainty in primary emissions, particularly for many hazardous air pollutants.
- Lack of systematic data on emissions and air quality for multiple pollutants in an integrated framework and database, supplementing the CP data.
- Scientific knowledge regarding the role of secondary processes for the formation of many air pollutants, such as photochemical oxidants and fine particulate matter including secondary organic constituents.
- Dearth of personal exposure monitoring data for many pollutants covering averaging times of interest, as well as lack of microenvironmental data and penetration rates of outdoor pollutants into indoor microenvironments.
- Extrapolation from ambient concentrations to personal exposures of ambient origin, particularly in the context of interpreting results from epidemiologic studies.
- Role of potential confounding by co-pollutants in evaluating the epidemiological evidence for individual pollutants.
- Role of effect modifiers in epidemiological studies; e.g., demographic and lifestyle attributes, socioeconomic status, genetic susceptibility factors, occupational exposure, and medical care.
- Concentration-response functions, including identification of potential population level thresholds and temporal stability of concentration-response functions.
- Effects of individual components of PM or mixtures of PM relative to their total mass concentration, combined with the presence of gaseous pollutants.
- Transferability or applicability of findings from an epidemiological study conducted in one location to other locations.

- Lack of multipollutant exposure and epidemiological studies, little knowledge of additive, synergistic or antagonistic interactions between pollutants, and lack of knowledge about societal preferences for differentiation of relative risks across pollutants.
- Time scales for recovery of ecological systems from apparent changes from atmospheric deposition.

While progress has been made in developing the models and tools necessary to conduct multipollutant risk analyses (e.g., development and application of the CMAQ and BenMAP models, and establishment and maintenance of monitoring networks for a range of pollutant species), challenges remain in informing and conducting these analyses. Some of the challenges are in the policy hierarchy, including the development of clear, specific, prioritized sets of objectives for multipollutant management, especially given the potential for tradeoffs (e.g., between an increase in risk for some populations and a decrease in risk for others that may occur when attempting to optimize emission reductions which potentially could increase or decrease ambient exposure by location). Others are technical in nature, and include the need to develop clear definitions of risk metrics and methods for combining and comparing risks across CP and HAPs pollutants. In addition, the challenges of integrating or prioritizing human health and ecosystem risk analyses remain quite formidable. Finally, some challenges are posed by the need to fill the most important gaps in the scientific knowledge that informs risk analyses. While the epidemiological literature is relatively large and robust in the United States and Canada, there are some important gaps in the available data on concentration-response functions for Mexico, especially away from Mexico City. Knowledge of vulnerable aquatic and terrestrial ecosystem response to reductions in pollutant deposition also remain limited in North America. To provide complete assessments of the economic (or other) benefits associated with risk reduction, a more complete and current set of estimates of the public's willingness to pay for reductions in risk for a variety of health and ecological outcomes need to be generated for all three countries (e.g., SAB 2007).

In all cases, improvements in the communication of the results of risk assessments are needed, especially for communicating uncertainty. Improved understanding of how decision makers use quantitative information from risk analyses is critical for improvements on how quantitative results are communicated. A forthcoming report from the recently established U.S. National Academy of Sciences/Institute of Medicine, Committee on Decision Making and Communication under Uncertainty, may provide useful insights in this area.

Key findings and recommendations on risk analysis include the following:

- *The existing risk analysis framework is conceptually well suited for analyzing multipollutant management actions*. Many elements of this framework, such as emissions and air quality modeling, already exist with multipollutant characteristics. However, the framework needs to be supported with information on exposure- and concentration-response relationships that result from multipollutant health studies;
- *Accountability and risk analysis are two realizations of the same risk framework.* Most risk analyses to date have been prospective in nature—estimating the

health or ecological risk reductions expected to occur as a result of a management action. Accountability involves a process of retrospective risk analysis—estimating the actual risk reductions that have occurred from implementation of a management action. Because the causal chain that links management actions to emission reductions, air quality improvements, exposure reductions and health outcomes is parallel between prospective and retrospective risk analyses, both types of assessment can and should be placed in a single risk management framework with common metrics and indicators where possible.

- *Goals and actions need to be defined in terms of risk metrics that are comparable across criteria pollutants and air toxics (hazardous air pollutants), and can encompass both human health and ecological risks.* These common risk metrics are essential to implement a risk-based multipollutant air quality management paradigm. While these metrics are challenging to develop, they are necessary in order to achieve multipollutant air quality management goals that meet public health and environmental needs in an effective and efficient manner, as conceived by the NRC (2004) committee.

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Chapter 5
Health Assessment Aspects of Risk- and Results-Based Multipollutant Air Quality Management

Joe Mauderly and Ron Wyzga

Knowledge of the health impacts of air contaminants is key to both the development of risk-based multipollutant air quality management strategies and the evaluation of their success in reducing the health burden of air pollution. This chapter summarizes the present ability of health sciences researchers to produce evidence useful for informing the development of multipollutant air quality management and assessing the resulting health benefits, the advances in knowledge and research strategies that will be required to substantially advance that ability, and realistic expectations for the next decade. The chapter reviews the scope of issues pertaining to the health assessment aspects of multipollutant air quality management, but it is not an exhaustive review of the literature supporting its premises. Citations are limited to examples that illustrate key points. The relevant literature is much more expansive than portrayed by these citations, and more information can be found in review papers (Samet and Krewski 2007) and texts, and in background documents developed by the World Health Organization and Canadian, U.S., and Mexican agencies to support specific air quality guidelines and regulatory actions.

Estimates of the health burdens of air pollution have been key drivers of regulatory actions to manage both ambient concentrations of high-volume pollutants of widespread distribution (the criteria pollutants [CPs] addressed in the United States by National Ambient Air Quality Standards, NAAQS, and similarly emphasized in Canadian and Mexican regulatory strategies) and other pollutants discharged by sources of more local concern, often termed hazardous air pollutants (HAPs) or air toxics. Concerns for human health have driven past air quality management practices more strongly than concerns for impacts on ecosystems, visibility, or climate change. Regardless of future priorities, it will be important to evaluate pollutant-health relationships closely because the pollutants of greatest importance for meeting health, ecosystem, visibility, and climate goals may differ. The conceptual goal of risk-based multipollutant air quality management is to reduce the total health

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burden from exposure to all environmental air contaminants. This chapter deals with key elements of the risk assessment framework described in Chap. 4, especially assessing exposure, identifying causal pollutants and combinations, and determining exposure-response relationships (potency factors). Continued progress toward supporting multipollutant air quality management will occur in incremental steps integrating increasing numbers of individual pollutants, pollutant groupings, and sources, and their corresponding health risks Accordingly, our confidence in developing multipollutant air quality management strategies and accounting for their success is inextricably linked to the confidence with which we understand links between various pollutants and health, and the confidence with which we can measure pollutant-related changes in the health impacts we seek to reduce.

It is important to note the context of this chapter. It is founded on the foreknowledge that: (1) exposure to air pollution can adversely affect human health; (2) all exposures to environmental air pollution are exposures to complex mixtures of pollutants that vary in time and space; (3) there are significant statistical associations between concentrations of individual criteria pollutants and population health outcomes, and the plausibility of these associations is supported by results from experimental exposures of humans, animals, and cells; and (4) the imprecision of exposure data for all pollutants, the sparse exposure data for non-criteria pollutants, and the lesser experimental attention given non-criteria pollutants preclude confident attribution of health effects among the full range of pollutants and their combinations to which people are actually exposed. Underlying the chapter is the assumption that the idealistic goals of risk-based multipollutant air quality management are to manage the full range of air pollutants, to maximize the total reduction of the pollution-related health burden, and to determine the success of air quality management strategies in reducing pollution-related health burdens. It is expected that progress toward these goals will be incremental and iterative and occur over several decades, and that the goals will likely never be achieved in ideal form.

The chapter is not intended as an explicit, step-wise roadmap for a multipollutant air quality management health research program; rather, it is an assessment of our present knowledge compared to the knowledge required to inform and assess multipollutant air quality management strategies. The chapter identifies key information gaps and the evolution of research strategies necessary to fill them. The interrelated hypotheses underlying this chapter are that: (1) portions of the health burdens associated statistically with individual criteria pollutants are likely to be shared among criteria and other pollutants; (2) non-additive interactions among pollutants, and between pollutants and other factors, are likely to underlie some health effects; and (3) substantial improvement in our understanding of air quality-health relationships is achievable with strategic attention to improving the scope and precision of exposure assessment and directing epidemiological and laboratory resources toward attributing health impacts among pollutants and their combinations. The consideration of these issues is not constrained to either the present regulatory framework or to specific future regulatory strategies; is it assumed that an evolution of regulatory structure can occur as warranted by improved knowledge.

5.1 Summary of Health Assessment Issues in Multipollutant Air Quality Management

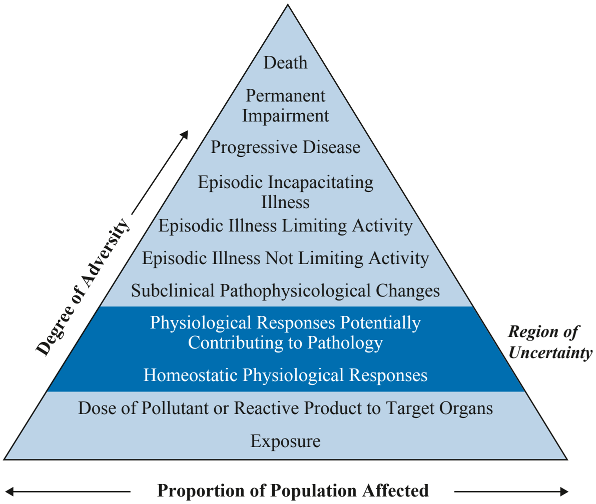
This chapter focuses on selected, inter-related issues of particular relevance to multipollutant air quality management. Although none of these conceptual and technical issues are new, the challenges they present are increased by a shift from the historic single pollutant, single source-oriented air quality management perspective to a truly integrated risk-based multipollutant air quality management framework.

5.1.1 Defining Adverse Health Effects and Target Populations

The need to identify effects warranting expenditure of resources to reduce or avoid risks is intrinsic to health-driven air quality management strategies. Knowledge of the range of health effects of air pollution and the proportional contribution of air pollution to those effects frames the prioritization of risk targets for multipollutant air quality management (as described in Chap. 4). Although formal and informal concepts of the "adversity" of different impacts of pollution on health have underlain past decision-making, it remains challenging to set definitive criteria. One aspect of the challenge is the continued expansion of the scope of health outcomes for which there is evidence of statistical associations with air pollution. The historic focus on respiratory function, lung defenses, and alterations of respiratory tract tissues has been complemented over the past decade by convincing evidence of cardiovascular effects (Brook et al. 2004; Künzli et al. 2005), increasing evidence of effects on lung growth (Gauderman et al. 2004; Rojas-Martinez et al. 2007) and gestational-developmental effects (Dugandzic et al. 2006), and suggestive evidence of effects in the brain (Calderón-Garcidueñas et al. 2007). It is not at all clear that we have yet identified the full range of adverse outcomes bearing statistical relationships to metrics of air pollution. Variation among the population in vulnerability to the effects of air pollution is another aspect of the challenge. In addition to long-held concerns for the very young, very old, asthmatics, and otherwise frail subpopulations, we are discovering genetic predispositions among apparently healthy adults (Schwartz et al. 2005). It can be anticipated that our knowledge of susceptibility factors and the resulting sensitive subpopulations will continue to expand, necessitating continued rethinking of the scope of health impacts warranting concern.

Perhaps the most challenging aspect of this issue is the fact that even given an outcome and a target subpopulation of concern, it is not straightforward to determine the point at which measurable impacts become sufficiently adverse to warrant air quality management-based intervention. This issue has been tackled before (ATS 1985, 2000), but is even less easily resolved now than in the past because of the increased scope of measurable biological markers. The impacts of air pollution encompass the continuum illustrated in Fig. 5.1. In decreasing order of severity, or "adversity", are death, permanent or progressive impairment, episodic illnesses that

Fig. 5.1 Relationship between of the degree of adversity of impacts of air pollution and the proportion of the population affected. The shaded area indicates the portion of the effects spectrum in which the adversity of effects is most uncertain



limit normal activity to various degrees, subclinical alterations signaling known or potential detrimental effects, normal protective physiological responses, doses of pollutants or their reactive products in target organs, and exposure to the pollutants. Arrayed against the numbers of people affected, this spectrum of adversity forms a triangle with the largest number of people exposed and manifesting little or no outward effect, and the smallest number comprising those whose deaths can be linked with some confidence to pollution exposure.

As discussed in following sections, there are uncertainties at both ends of the adversity spectrum; i.e., concerning both the heterogeneity of personal exposures and the contribution of exposures to death. However, there is an especially challenging region of uncertainty concerning the prioritization of biological responses that can be measured in increasing detail, but are of uncertain linkage to clearly adverse outcomes. Our ability to monitor the myriad chemical, neural, and other normative adjustments to our personal environment at the molecular, cellular, and organ levels has increased markedly, but this evolution in technology has done little to clarify points at which responses are "adverse", or sufficiently important to warrant intervention.

The above considerations have important implications for the difficult, but important, issues of evaluating exposure-dose-response functions and the existence of thresholds for adverse effects. These issues are not unique to multipollutant air quality management; they are also important to estimating the impacts of single pollutants. However, the importance of dose-response at low exposure levels is heightened when attempting to disentangle the combined effects of multiple pollutants when each is present at a low concentration. It is not difficult to envision direct relationships among exposure, ventilation patterns and levels, and dose to target sites, although gaps in our understanding of the dosimetry of many pollutants remain. It is much more difficult to define responses that are worthy of avoidance and acceptable thresholds for adverse responses. Considering the triggering of normative physiological responses to exposure (region of uncertainty in Fig. 5.1) as an adverse effect precludes the possibility of a clear biologically-based threshold, because the body is continually adjusting to its environment and we have an increasingly sophisticated ability to monitor these adjustments. It is not surprising that epidemiological research cannot define statistically significant thresholds for observed outcomes, because of the uncertainty of exposure assignment in population studies and the diversity of susceptibility within the populations. It is not possible to reduce the concentrations of most man-made pollutants to zero, even under the most stringent regulatory approaches. Despite differences in viewpoints, it is universally understood that practical thresholds for managing exposures must be adopted. It continues to be extremely challenging to implement legislative (as well as unstated) mandates to protect the most sensitive individuals.

5.1.2 Apportioning Effects Among a Broad Range of Pollutants and Combinations

Significant progress toward a truly integrated multipollutant air quality management goal of achieving the greatest aggregate reduction of risk per unit of air quality management resources requires knowledge of which pollutants drive the different health effects and whether there are important combinations of pollutants whose effects are greater than additive. Past research approaches have identified exposure-response relationships guiding air quality management strategies aimed largely at a small number of individual pollutants; however, they have provided only a modest basis for apportioning effects among the much broader range of pollutants that people actually breathe or for assessing the importance of combinations (Goldberg 2007). Consideration of multiple pollutants in epidemiological studies has largely been aimed at sharpening risk factors for individual pollutant species by examining the effects of including commonly measured co-pollutants in models (Samet et al. 2000a). Only a few studies have acquired the data to examine the effects of pollutants beyond those measured routinely (Metzger et al. 2004). As described in following sections, improving our knowledge base substantially will require a shift in research emphasis toward a more systematic evaluation of the effects of a broader range of pollutants.

The consideration of combined exposures to multiple pollutants necessitates consideration of the different interactions that might occur among pollutants (see Text Box 5.1). In the absence of information to the contrary, the default assumption is that the effects of combinations of pollutants are additive. That is, for any given health outcome, the effect of the mixture is the sum of the independent individual effects of the components. If the “effect” is an observed health outcome at the functional level (e.g., symptoms, exacerbation of asthma, cancer), different causal pollutants might contribute to the effect by influencing different steps in the biological pathway by which the effect is caused. If the “effect” is observed at the cellular or molecular level (e.g., increase in blood levels of a certain DNA or protein

Text Box 5.1 Potential Interactions Between Pollutants*

Additivity:	effect of the combination equals the sum of individual effects
Synergism:	effect of the combination is greater than the sum of individual effects
Antagonism:	effect of the combination is less than the sum of individual effects
Inhibition:	a component having no effect reduces the effect of another component
Potentiation:	a component having no effect increases the effect of another component
Masking:	two components have opposite, cancelling effects such that no effect is observed from the combination

*"Effect" means the observed expression of the particular health outcome in question. A combination of pollutants could have different interactions for different outcomes. The interaction could occur at any level of biological pathway from exposure to expression of the outcome. (From EPA 2000)

adduct), it is more likely that causal pollutants act by the same mechanism. Some of the potential interactions listed in the text box are known to occur, while others are possible, but not documented. Only a few combinations have been studied in the laboratory and the issue has received scant attention in epidemiological studies. However, results to date suggest that the effects of combined exposures are as often less additive than they are synergistic (Mauderly and Samet 2009).

5.1.3 Improving Estimates of Exposure

Improving estimates of exposure will be an important component of refining our knowledge of the range of effects of air pollution, causal pollutant species, and exposure-response relationships. As described in Chap. 4, estimates of human exposure are integral to risk assessment. Determinants of exposure include the concentrations of pollutants in the different exposure environments and the times spent by individuals in those environments. The activity levels of the individuals during those times is also important for estimating the relative "doses" of pollutants received in the different environments. The current effort to derive exposure terms for epidemiological studies by modeling local concentrations from scattered air monitors, meteorology, and source location (Jerrett et al. 2005a) will need to be complemented by greater effort to characterize pollution in different microenvironments, and model personal exposures of target subpopulations by defining representative time-activity patterns and linking them to concentration data (Georgopoulos et al.

2005). The importance of understanding the heterogeneity of exposure among places and people will likely increase as the number of target pollutant species increases.

5.1.4 *Estimating the Proportional Contribution of Air Pollution to Health Burdens*

With few (if any) exceptions, air pollution is not the sole cause of the mortality or morbidity outcomes with which it is associated statistically in exposed populations. The outcomes can be caused by other factors independent of air pollution, and other factors also contribute to the expression of outcomes that are affected by pollution. Especially when global health burdens are considered, air pollution may be a minor contributor to some health outcomes with which air pollution is commonly associated (Cohen et al. 2005). Controlled exposures and panel studies can draw more definitive links between exposure and effects, and are important to establishing causality and defining quantitative exposure-response relationships. However, confirmation of causality does little to clarify the portion of that health burden that is caused by air pollution. Increasing emphasis on assessing the benefits of air quality management places increasing importance on understanding the proportional contribution of air pollution to the different health outcomes. Estimates of proportional contributions are especially important to setting realistic expectations for the magnitude of measurable benefits of pollution reduction strategies.

5.1.5 *Evaluating the Health Benefits of Multipollutant Air Quality Management Strategies*

The traditional approach to cost-benefit analysis of air pollution mitigation strategies links concentration-response functions of adverse pollution-related health effects with predicted changes in pollution concentrations attributable to the mitigation strategy. This approach inherently assumes that the pollutants of interest are directly causing the health effects and changes in pollutant concentrations will in fact lead to changes in population health status. However, several factors can change over time. Members of that population may alter their time-activity patterns to purposely or coincidentally change their profile of exposure to the pollutants of interest. The prevalence of diseases most closely linked to air pollution may also change due to changes in other causes. The nature of the pollution mixture and other atmospheric conditions may change with time. This last point is especially critical when mitigation strategies are focused on reducing the mass concentrations of respirable ambient particulate matter (PM). There is a multitude of diverse particulate pollutants in the atmosphere and the relative contributions of the different components of PM to health outcomes are not well-known. Because simply reducing total PM mass may not efficiently target the most toxic components, there may be no assurance that population health will be improved in direct proportion to reductions of PM mass. Methods need to be developed which can track changes in air pollution-related health effects over time in relation to changes in atmospheric pollution levels in order to assess the population health benefits of mitigation strategies. A first step would be to demonstrate that management strategies have resulted in reduced exposure. Subsequent steps would test relationships between reduced exposure and reduced health impacts.

5.1.6 Setting Realistic Expectations

It is important to frame realistic expectations for the extent to which the exposure and health communities can currently inform multipollutant air quality management strategies and assess their effectiveness, and the rapidity with which these capabilities can be improved. Air quality management strategies already consider multiple pollutants to a limited extent, but are founded almost entirely on estimates of the health implications of individual pollutant species or sources. As described in following sections, substantial improvement in our ability to parse the effects of different pollutants and integrate health impacts from complex pollution exposures will not only require the will to do so, but also substantial time and resources.

5.1.7 Non-inhalation Impacts

Although this chapter focuses on health effects of inhaled air contaminants, air contaminants also have impacts on health via other exposure pathways. Ignoring multimedia exposures could lead to an underestimation of the total risk from air pollutants. To the extent that air pollution contributes to climate change, it must also be acknowledged that climate change can impact human health. The following examples of non-inhalational effects are provided here, but are not expanded in later sections.

Ingestion of Contaminants Introduced into the Environment as Air Pollutants. Humans are exposed by ingestion to traces of hazardous species deposited on structural surfaces, plants, soil, and water by airborne transmission. A few classes of air contaminants have raised concerns for this route of exposure. Historically, lead-based fuel additives raised lead levels in soil and on surfaces near roadways, which contributed to exposure by ingestion (Davis et al. 1993) as well as resuspension. A portion of the contaminants in river and estuary sediments, and thus in fish and shellfish, are undoubtedly deposited from air (Ritter et al. 2002). Pesticides and herbicides applied as sprays can lead to human exposure by ingestion (Alegria 2006).

In recent years, mercury has received more attention than any other contaminant for its contribution to human exposure through ingestion. Ingestion of mercury, primarily in fish, is the principal route of exposure to this contaminant, and has been associated with neurological effects and possibly cardiovascular effects. There are several sources of mercury in the environment, but the regulation of airborne emissions has focused on combustion sources, primarily coal combustion and waste incineration.

Health Impacts of Climate Change. Increased temperatures will produce several direct and indirect health consequences: heat-related mortality and morbidity; effects of increases in certain air pollutants (e.g., ozone); increases and broader distributions of insect and rodent-borne diseases; increases and broader distributions of certain water and food borne diseases; and the effects of extreme weather events such as storms, tornadoes, hurricanes, floods and droughts. For example, epidemiological data from different states of Mexico have shown that rates of disease have increased with temperature in places where the illnesses are endemic. An increase of 1°C was associated with 1.15 and 1.6% increases in cases of malaria in Chiapas and Sinaloa, 1.5–2% increases in cases of dengue in Colima and Guerrero, and a 1.97% increase in cases of diarrhea in Chiapas and Puebla (INE-SEMARNAT 2006).

Relationships Between Ecological and Human Health. Air pollution affects ecosystems (addressed in Chap. 6), and ecosystems have significant direct and indirect impacts on human health. Vegetation captures and fixes carbon, facilitates the infiltration of water into aquifers, filters PM from air, removes carbon dioxide, and generates oxygen. Vegetation also moderates climate, stabilizes soils, produces food and building materials, and enhances recreational and aesthetic values. Loss of forests and desertification in rural areas has obvious impacts on indigenous populations; however, urban populations are also affected by ecosystem deterioration. In Mexico City, for example, 60% of the total land area is undeveloped "conservation area," and the deterioration of these ecosystems by ambient air pollution have adversely affected the health and welfare of the population (Fenn 2002; Ruiz-Suárez 2007).

5.1.8 Similarities and Differences Among Canada, Mexico, and the United States

The air quality management approaches of the three NARSTO countries and their current air quality guidelines and standards were summarized in Chap. 3. There are both similarities and differences among the countries in priorities and strategies for air pollution exposure and health effects research, the collection and availability of public health data, and the resources allocated to these efforts. The issues, information needs, and research approaches associated with multipollutant air quality management are common among the countries, and it is useful to briefly compare some of the factors that will underlay movement toward multipollutant air quality management in the three countries.

Populations. The health effects of air pollution can be influenced by several demographic, socioeconomic and health factors. Both the very young and elderly populations have been shown to be sensitive to air pollution exposure. For example, a time series study of infant mortality suggested an important increment for the young population compared to older people. (Loomis 1999). The underlying disease status of the population also influences the impact of air pollution on health. Socioeconomic status has been shown to influence health responses (Krewski et al. 2000; Romieu et al. 2004a). In some studies, most of the apparent differences in air pollutant effects found among races and geographic areas could be explained by socioeconomic and/or health care disparities, the effect of which could be enhanced by air pollution (Gwynn and Thurston 2001).

Table 5.1 briefly summarizes some of the differences and similarities in population factors for the three countries. The table must be qualified by the fact that there is not a uniform method of collecting and reporting data among the three countries.

At this time, the population of Mexico differs from those of Canada and the United States more than the populations of the latter two countries differ from each other. The Mexican population is younger than those in Canada and the United States, which raises special concern for the effects of pollution during gestation and in young children (Romieu et al. 2006b). Mexico has a high level of social inequity and a large percentage of the population is poor in both rural and urban areas. In 2002, one-fifth of the population was in extreme poverty (World Bank 2009). Poverty and social inequity influence many aspects of society, including: employment level and access to productive resources; limited access to education, health care and other public services; vulnerability to economic risks; limited voice, power and participation in decision-making; and lack of a healthy physical living environment (Sen 1999; Kawachi and Wamala 2007). These variables can affect vulnerability to air pollutants.

Table 5.1 Comparison of selected demographic parameters among the three North American countries

	Canada	Mexico	United States
Percent 0–14 years	17.7	31.0	21.4
Percent 60+ years	17.9	7.8	16.7
Source: Pocket World in figures, 2007 ed., The Economist, London			
Percent children in urban areas	80	75	80
Source: Commission for Environmental Cooperation, 2006			
Percent tobacco use (males)	22	35.9	24.1
Percent tobacco use (females)	18	15	19.2
GNP per capita (PPP $)	32,220	10,030	41,950
Infant mortality/1000	5	22	7
Source: World Health Statistics 2007			
Life expectancy			
males	78.2	73.7	75.2
females	83.1	78.6	80.6
Source: Pocket World in figures, 2007 ed., The Economist, London			

Pollution. Air pollution health effects research and the health-based standards of the three countries have largely considered the same criteria pollutants,[1] and the methodologies used to assess the health effects of these pollutants have been similar. Indeed, there has been considerable communication and collaboration among epidemiologists and laboratory scientists of the three countries. The pollutants of concern are the same in all three countries, although the pollutants dominating health concerns vary from region to region. The three countries have all made extensive use of air quality data collected largely for other purposes to examine pollution-health relationships, and the nature and availability of monitoring data has posed similar challenges to their use for epidemiological studies. The countries share an improving, yet still inadequate, ability to assess the effectiveness of air quality management strategies in reducing the health burdens of air pollution (termed regulatory "accountability").

There are national and regional differences among the three countries in predominant sources and predominant concerns. In its report, "Taking Stock 2003" (CEC 2006), the Commission for Environmental Cooperation reported that, based on emission inventory data, electrical utilities were the largest source of nitrogen oxides (NO_x) in all three countries; however, the latest EPA inventory of emissions (EPA 2007) indicates that (on-road and non-road) diesel engines are currently the largest source of NO_x emissions in the United States. With respect to sulfur dioxide (SO_2), electrical utilities were also the largest source in both Mexico and the United States, but primary metal industries represent the largest source in Canada. The largest stationary sources of volatile organic compounds (VOCs) were the oil and gas extraction sector in Canada, chemical industries and petroleum refining in Mexico, and a combination of miscellaneous fuel combustion, petroleum processing, industrial processing, paper products and hazardous waste management in the United States. Vehicle emissions are a pervasive source of exposure to PM, NO_x, carbon monoxide (CO) and VOCs in all three countries. Ozone generated from NO_x and VOC precursors is an important health concern in all three countries.

Both the mixture of pollutants and pollution levels vary considerably among regions. Differences in geography and meteorology, as well as sources, lead to some differences in pollution levels and composition among the three countries. Ozone, for example, tends to be more prevalent in warmer, sunnier areas, although high ozone levels occur in certain cooler locations. Drier climates, as are typical in much of Mexico and the southwestern United States, are associated with higher exposures to resuspended crustal PM. In some areas, this material contains a variety of compounds that have not yet been well characterized, nor have their effects on human health (Rosas-Pérez et al. 2007; Osornio-Vargas et al. 1991). Differences among the countries in combustion sources and fuels may also lead to differences in exposure and health risks. In Mexico, for example, there are larger populations exposed to biomass smoke during cooking than in Canada and the United States,

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[1] The lists of air toxics (hazardous air pollutants) differ by country and are defined in the List of Terms.

and the diesel fuel in Mexico has a higher sulfur content than in the United States and Canada.

The three NARSTO countries share similar air quality objectives, but the collection of air quality data is not uniform among them. In Mexico, for example, air quality data have not been collected in medium and small cities (INE 2007) as it has in Canada and the United States. Monitoring for non-criteria pollutants is limited in all three countries. In the United States, there is a monitoring program for all of the officially designated 187 HAPs, but the program is very limited in scope.

Health Impacts. Epidemiological evidence of pollution-health relationships is generally similar among the countries, but some interesting differences contribute to the complexity of integrating results and conclusions among countries. For example, a time series mortality study (Castillejos et al. 2000; Loomis et al. 1999) suggested that particles are more toxic per unit of mass for infants and old people in Mexico City than in American and Canadian cities. Attempts at evaluating the benefits of air quality management have been more common in Canada and the United States than in Mexico, although improvements in air quality in Mexico provide good opportunities for such studies. For example, the health benefits of the considerable reductions of ozone and PM in Mexico City have not been properly evaluated, although the Milagro Campaign in Mexico, which includes the study of non-criteria pollutants, has provided valuable data (Molina et al. 2007).

Support for Air Pollution Research. There are differences among countries in the amount of federal resources directed toward pollution research and mitigation. The primary source of peer reviewed health research grants in Canada is the Canadian Institutes of Health Research (CIHR). A search of the CIHR-funded research database from 1999 to present revealed total grants of $ 4.3 million for the term “air pollution.” Additionally, the time-limited Toxic Substances Research Initiative (TSRI) allocated $ 7.2 million for urban air quality between 1999–2002, the Border Air Quality Strategy (BAQS) provided approximately $ 23 million between 2003 and 2007, and the Program of Energy Research and Development (PERD) administered by Natural Resources Canada, provided $ 2.6 million for the period 2000–2009.

In Mexico, there are two major sources for health research grants: CONACYT (The Science and Technology Council) through what is called Sectorial Funds; and FUNSALUD (Health Mexican Foundation). The amount of money dedicated specifically to air pollution and health research is uncertain, but in 2004 and 2005 these programs provided 1,423 and 1,951 million Mexican pesos, respectively, for the health sector. Most of the air quality health research in Mexico has been supported by international agencies from the United States, Europe, and in a limited quantity by the Pan American Health Organization (PAHO). The National Institute of Ecology (INE) has supported efforts to monitor regulated pollutants in 9 large Mexican cities, and data are available for the last five years. Since 1988, there has been an extensive effort by the local government in Mexico City to measure criteria pollutants, and INE is also measuring some hydrocarbons and other toxics. Few health studies have been conducted outside Mexico City due to the lack of complete and precise monitoring data in other cities.

No single entity within the United States has authority to manage air pollution research. The federal government, through EPA and the National Institutes of Health, is by far the largest sponsor, with an annual budget of about $ 43 million (NRC 2004). The Air Quality Research Subcommittee of the interagency Committee on Environment and Natural Resources Research facilitates communication among agencies about air quality-related issues (www.gcrio.org/USGCRP/CENR/), but the research is not well-coordinated among the different agencies. Outside the federal government, research is funded by the Health Effects Institute, using funds from EPA and industry, and by industry associations, non-profits, or individual corporations. Although there is general awareness among these federal and non-federal entitities of the scope of activities of other sponsors, there is no formal mechanism for coordinating efforts.

5.2 Current Understanding of the Relationships Between Air Quality and Health

Our current understanding of the impacts of air quality on health derives largely from research aimed at single pollutants, pollutant classes, and sources. Although much is known, it is necessary to evaluate our current understanding of relationships between air quality and health in light of our ability to advise and evaluate multipollutant air quality management strategies. This section accomplishes that in summary form.

5.2.1 Sources of Information

5.2.1.1 Epidemiology

Epidemiological evidence has a central role in the development of air quality management strategies to protect the public's health. The dramatic air pollution disasters of the twentieth century—the Meuse Valley in 1933, Donora, Pennsylvania in 1948, and the London Fog of 1952—provided clear indication of the potential for high levels of air pollution to cause excess mortality and morbidity. While the health consequences of these episodes were evident simply by tracking deaths, the science of epidemiology has long served as the basis for assessing the adverse effects of air pollution on the public's health at more routine levels of exposure. Since the 1950s, epidemiological research has provided the evidential foundation for setting standards for several pollutants, particularly particulate matter, while laboratory-based findings have been more critical for others, including carbon monoxide and ozone. Epidemiological evidence is interpreted and applied within the context of the findings of other lines of research, including animal and human toxicology studies and mechanistic studies.

Study Designs. The health effects of air pollution are studied in communities using observational designs that assess the effects of air pollution by examining associations of risk for adverse health effects in relation to being exposed versus not exposed or to the level of exposure. Epidemiological studies are designed to take advantage of gradients in exposure that occur spatially or temporally. The effects of air pollution are typically estimated as the increase in risk for the health outcome of interest in relation to a change in exposure; e.g., the percentage increase in mortality per 10 μg/m^3 increase in PM concentration. The major study designs used in epidemiological research are classified by the timing of the investigation of the association between exposure and disease risk (prospectively, retrospectively, or simultaneously) and by the study population (individuals or groups) (Gordis 2004). Figure 5.2 illustrates these design concepts, showing how the major designs assess the exposure-disease relationship. A cohort study examines this relationship prospectively by tracking exposed and non-exposed persons; in a case-control study the assessment is retrospective and in a cross-sectional study it is simultaneous.

In cohort studies, participants are selected and exposures characterized and they are followed forward in time with monitoring of disease occurrence. The Harvard Six Cities study exemplifies this design (Dockery et al. 1993). In 1975, the study began with enrollment of children and adults in six communities in the United States. Over the ensuing years, the participants were actively followed with measurement of lung function and tracking of respiratory symptoms and with identification of deaths. Levels of key air pollutants were also monitored during the follow-up. In cross-sectional studies or surveys, exposures and health indicators are assessed at only one point in time, on the assumption that the finding of adverse health effects reflects exposures prior to the time of observation. This design has been used, for example, to compare respiratory health between persons living in more and less polluted communities that are otherwise similar. The case-control design involves comparing the exposures of persons with a disease under study (the "cases") with

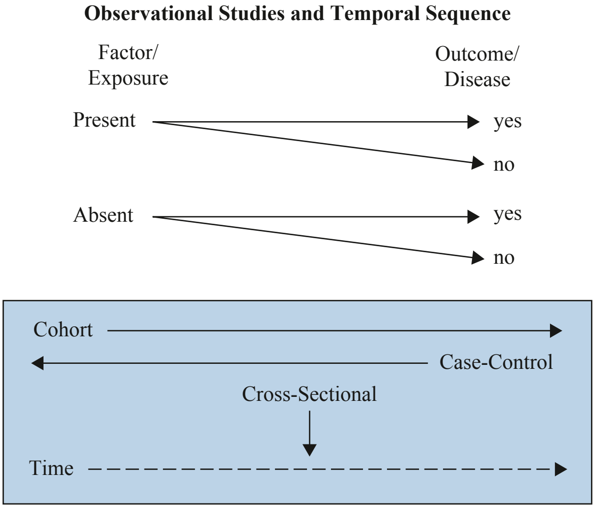


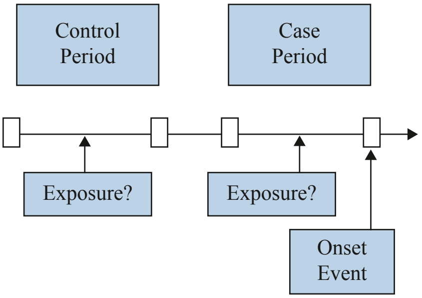
Fig. 5.2 Relationship between exposure and the time of study for three fundamental types of epidemiological studies

the exposures of similar persons without the disease (the “controls”). This design has had little application in studying air pollution, except for addressing the contribution of air pollution to the occurrence of chronic diseases, such as lung cancer.

Ecological study designs have groups of people, such as residents of a particular city, as the unit of observation rather than individuals. Air pollution exposures are estimated for the group and disease occurrence is assessed within the group as exposure varies over time (the time-series design) or across groups having different exposures. In the widely used daily time-series design, risk for the health outcome on a particular day is assessed in relation to air pollution levels on that day or on recent days. Over the last decade, a number of multi-city time series studies have been conducted, such as the United States National Morbidity, Mortality and Air Pollution Study (NMMAPS) (Samet et al. 2000a, b). In this approach, time-series analyses are carried out within multiple cities using a standard method for the analysis, and the data from the individual cities are then compared and combined if the associations are similar across cities. This approach is more statistically powerful than analysis of data from a single city and it facilitates comparisons of results among cities.

The case-crossover design is another approach to time-series analysis (Mittleman et al. 1995). It is not an ecological design, but is based on individual estimates of exposure. In this design, exposures are compared in a “case period”, an interval of time considered to be biologically relevant to the occurrence of the health outcome and during which the outcome event occurs, to exposures in one or more “control periods,” that is, time periods when the study participant was at risk for both exposure and outcome, but an event did not occur. This design, originally described in the early 1990s, has been used to assess very short-term exposures to air pollution and risk for cardiovascular and other health outcomes (Mittleman et al. 1995). For example, Symons et al. (2006) used this approach to assess air pollution and risk for congestive heart failure (Fig. 5.3), Peters et al. (2004) used it to assess risk for acute myocardial infarction from traffic exposure, and Schwartz (2004) used it to estimate effects of PM vs. those of other criteria pollutants.

While observational epidemiological studies are generally classified as based around either individuals or population groups, some studies have elements of both;



The **Case Period** is the exposure period before an event. It can be found empirically but must be biologically relevant to the association of interest.

The **Control Period** can be:

a. exposure information from a comparable time period,

b. past exposure information according to an individual’s usual frequency of exposure, or

c. multiple control periods can be used (~n : 1 matching)

Fig. 5.3 General case-crossover design for linking exposure to health outcomes a design that has been referred to as “semi-ecologic” (Künzli and Tager 1997). In the Six Cities Study, for example, information was collected about disease risk factors and demographic characteristics for individuals, but air pollution exposure was assigned by community of residence. Thus, the number of observations for estimating the risks of air pollution was only six—the number of cities—rather than 8,111, the number of individual participants (Dockery et al. 1993). This design has the strength of facilitating controls for factors other than air pollution, which vary across individuals.

Observational studies of air pollution have well-known limitations reflecting potential bias from participant selection (selection bias), error in classifying exposure (exposure misclassification), uncontrolled effects of other factors (confounding), or an insufficient sample size leading to lack of statistical power. These potentially limiting features of epidemiological evidence are given strong consideration in the design and analysis phases of an investigation in an effort to minimize their consequences. Some sources of systematic bias may increase or decrease the apparent effect of air pollution, while random errors, particularly in exposure and outcome assessment tend to reduce apparent effects.

Challenges in Determining True Exposure-Risk Relationships. Exposure classification is a particular concern in studies of air pollution and health (Zeger et al. 2000). In epidemiological studies, the conceptual ideal would be to have accurate exposure estimates for each study participant. This ideal is rarely achievable and instead, exposure indicators are used that provide estimates of individual exposure that are subject to error. The approaches generally used, described below, have associated errors that may be systematic or random. Misclassification may occur when exposures are categorized for individuals based on indicators measured with error. If the misclassification is random in relation to the risk for the health outcome, it is generally true that the study underestimates the true association between exposure and outcome. To address the consequences of measurement error, researchers may include a validation sub-study into the main data collection so that the extent of misclassification arising from the exposure measure can be assessed against a measurement that is considered more accurate and that is made for a sample of the subjects.

Confounding is another bias of concern in studies of air pollution. It occurs when a confounder, a risk predictor for the outcome of concern, is also associated with the air pollutant under investigation. For example, in a cohort study of respiratory health, the prevalence of cigarette smoking might be correlated with estimates of exposure to PM, if persons with higher exposure to air pollution had different smoking patterns compared to those with lower exposure. Confounding may increase or decrease the degree of association. The potential for confounding should be a consideration in the design of a study, so that information is collected prospectively on potential confounding factors. It can be addressed in the analysis by stratifying the data by the confounding factor, and also by using multivariate models which make adjustments for the confounding factors. The success of such models depends on the availability of data on the potential confounding factors and the appropriateness of the model to represent the relationships among the confounding and exposure variables. If not adequately addressed, confounding may introduce association that could either increase or decrease the apparent effect of air pollution.

The interpretation of epidemiological studies may also be clouded by imprecision of risk estimates, leaving open the possibility that an apparent association between air pollution and risk for a health outcome has arisen by chance. The intended degree of precision with which effects are to be estimated is one consideration in determining the needed sample size when designing a study. However, the target sample size may not be achieved because of feasibility considerations or because a sufficiently large sample size is not available. The imprecision of estimates is manifested by the confidence intervals, which bound the range within which the true effect is likely to lie, at the specified level of confidence, e.g., 95%.

Evaluating Effects of Multipollutant Exposures. These epidemiological approaches have been used to study the effects of multiple pollutants, particularly the criteria pollutants. These pollutants, of course, are present in mixtures and have shared sources; some of the primary gaseous pollutants have a critical role in the formation of secondary pollutants. Both sulfur oxides and nitrogen oxides contribute to respirable particles. Nitrogen oxides, along with hydrocarbons, are involved in the generation of ozone through photochemical processes. Because of the interrelationships among pollutants, their common sources, and the influence of meteorological conditions on their concentrations, the "independent effects" of the pollutants can not readily be estimated.

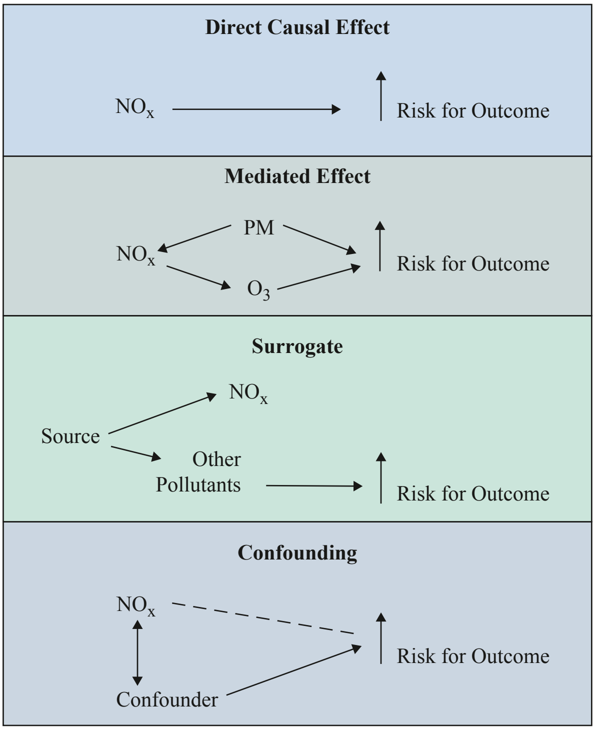
The general approach for doing so is to use multivariate regression models that incorporate terms representing each of the pollutants of interest; if the correlations are not high among the pollutant variables, then effects of the pollutants can be estimated by fitting the specified model to the data. However, interpretation of such models can be difficult as noted. As mentioned above, NO_x provides a good example by contributing to secondary particle and ozone formation, and affecting health through these pathways (Fig. 5.4). Statistical models are challenged to separate effects mediated via these indirect pathways from effects resulting from direct causation.

There is the further complication that the individual pollutants may interact in synergistic or antagonistic ways or that the risk of the mixture may not be adequately estimated by effects estimated for the individual pollutants. Epidemiological analyses can search for such interactions, typically assessed by adding product terms among individual pollutants into models and testing whether model fit to the data is enhanced as a result. Such analyses have limited statistical power and are model-dependent in their representation of how pollutants may act together mechanistically. Their interpretation is further complicated by the inherent errors in estimating pollution exposures and the possibility that the degree of error varies from pollutant to pollutant (Samet and Speizer 1993).

How can epidemiological studies provide information on the risks of "real-world" multipollutant mixtures? This topic has been considered in many workshops without resolution. Potential approaches include:

- Rigorous characterization of the multiple pollutants of concern within one community over time, or in multiple communities having contrasting pollution patterns; analysis with multivariate models with exploration of interactions; and summing of the effects of the individual pollutants and of their interactions;

Fig. 5.4 Potential relationships of NO_2 with adverse health effects



- Multi-city studies that span a range of pollutant sources and concentration patterns, using analyses directed at variation in effects across different pollution profiles. These studies should not obscure differences in associations among the locations, but should utilize differences to make inferences about air pollution-health relationships.; or
- Measurement and analytical use of biologically-based markers, e.g., of oxidant stress. Such methods are under development.

Regardless of the approach, researchers should look for opportunities to use hybrid approaches that bring toxicology and epidemiology together in the population context.

5.2.1.2 Exposure Specification

Our understanding of exposure-response relationships can be no better than our understanding of exposure. The fundamental challenges of estimating exposures are not unique to multipollutant studies; the same general issues pertain to studies of the effects of single pollutants and source emissions. There is need for more precise exposure specification even for single-pollutant studies. Issues bearing on the precision of exposure estimates become even more critical, however, in exposure assessments in studies aimed at determining the relative effects of many individual pollutants present as mixtures. This is especially true for pollutant species and classes that are present in low concentrations in ratios that vary significantly among exposure environments.

Estimating Personal Exposure. Exposures are complex, and can vary widely among individuals. People are exposed to pollutants both indoors and outdoors during the course of a typical day (e.g., indoors and outdoors at residences, while commuting, at schools and workplaces, etc.). Pollutants are generated by a wide variety of indoor and outdoor sources, including stationary and mobile sources, building materials, consumer products, and atmospheric reactions among precursor emissions. It is not necessary to understand the sources in order to evaluate exposure-response relationships if exposures are measured directly; however, it is necessary to understand source contributions if exposures are to be modeled from source emissions or if exposures are to be controlled by regulating source emissions. To do this, it is important first to determine the relative contributions of different sources to concentrations of pollutants in microenvironments of importance for the individuals or population groups of concern (e.g., children, elderly, susceptible sub-groups). Contributions to personal exposures from indoor or outdoor sources may be estimated using information from monitoring studies and time-activity surveys. Time-activity data allow estimation of exposure durations and delivered dose using physiological data and exertion level information. In conjunction with micro-environmental concentration measurements, time-activity data enable estimation of exposure doses and the time-sequence of personal exposures using mechanistic exposure models, such as the SHEDS (Stochastic Human Exposure and Dose Simulation) model (Özkaynak et al. 1996; Burke et al. 2001).

In the absence of personal exposure measurements, air pollution epidemiology has traditionally relied upon imperfect surrogates of personal exposures, such as readily-available data from central site outdoor monitors (Özkaynak et al. 1986, 2007). The accuracy of surrogates for assessing the pollutant of concern can vary among pollutants, and those differences can impact the results of statistical analyses. Moreover, the ability to attribute exposures to different types of mobile, major, area, and background sources has also been limited. Experience to date has mostly been with pollutant-specific empirical or atmospheric dispersion models applied in the context of ambient pollution concentration-response analysis (Jerrett et al. 2005b; McConnell et al. 2006; Molitor et al. 2007).

Researchers have more recently begun using a variety of space- and time-resolved atmospheric models and micro-environmental personal exposure modeling tools (Isakov and Özkaynak 2007; Burke et al. 2001; Özkaynak et al. 2007; Isakov et al. 2006). The information needed to run some of these models can be extensive, including data for time-activity patterns, concentrations in microenvironments, air exchange and heating, ventilation, and air conditioning, housing, and other physical factors, and consumer product use. Much of the current challenge lies in improving the amount and quality of this information.

Air Quality Indices as Exposure Terms. An air quality index (AQI) is a numeric scale intended to reflect the quantity of air pollution present at a given point in time, and its health significance. It is often reported with respect to both current and forecasted conditions. Numerical AQI values are often accompanied by color schemes, category labels (e.g. “good”, “fair”, “poor”), and health advice. Most AQIs currently in use around the world are calculated by comparing each pollutant in the index to its standard, and reporting the index as the number corresponding to the pollutant which is highest relative to its standard. This approach has recently been criticized because it does not capture additive effects of multiple pollutants, or reflect the apparent no-threshold concentration-response relationship which characterizes the association between air pollution and health. Cairncross et al. (2007) and Stieb et al. (2008) recently described the application to AQIs of concentration response functions from epidemiological studies to address these criticisms.

Epidemiological studies of air pollution almost always quantify effects strictly in terms of concentrations of individual pollutants, although in many cases, effects are examined in both single and multipollutant models (i.e. single versus multiple pollutant terms in a regression model). Rarely, effects are examined in terms of a weighted combination of pollutants as in principal components analysis (Burnett to et al. 2000; Holberg et al. 1987; Smith et al. 2000) or using an existing air quality index as an independent variable (Kesten et al. 1995). Given the regulatory focus on individual pollutants, investigators may see little reason in epidemiological studies to quantify effects of combinations of pollutants as in an AQI. Because AQI formulas differ among jurisdictions, reporting effects according to a particular formula may have limited generalizability.

Differences in Availability of Data for Criteria and Other Pollutants. Ambient air quality data are generally collected for criteria pollutants that are regulated by ambient concentration, especially in those areas where levels may be exceed standards. These measurements are seldom, however, made on a daily basis. Ambient concentration data are not typically available for pollutants, such as HAPs, that are regulated by emission standards, or for species that are not regulated. The EPA speciation network measures some particulate HAPs, but not daily, and organic HAPs vapors are measured by the Photochemical Assessment Monitoring Stations (PAMS) network. Lack of daily data makes it difficult to study the potential health impacts of pollutants that are not routinely measured, and thus it is difficult to determine the need to regulate them.

Importance of Biological Time Scales. The time scales over which the biological effects of interest may occur must be considered in developing an appropriate measurement- or modeling-based exposure prediction strategy, and biologically relevant time scales of exposure vary among the different classes of pollutants (McKone et al. 2007). Exposure data with fine time resolution are needed when acute effects are of interest; however, short-term studies (hours to weeks) are not very informative for assessing health risks due to long-term exposures. The influence of time scales can become more complicated when synergies or other interactions among pollutants may differentially influence the responses observed for each of the individual pollutants. This is an important consideration, for example, in the investigation of the role of mobile-source air toxics or VOCs in health effects associated with PM and co-pollutants near-roadways (Brugge et al. 2007; Brauer et al.

2007; Hoek et al 2002). Biological time scales must be considered in evaluating the role of air toxics (e.g., VOCs) in the exacerbation of acute respiratory symptoms associated with exposures to particles and gases, versus their role in the development of cancer and other chronic diseases. When evaluating the health risks from exposures to multiple pollutants, both the characterization of exposure and the measurement of effects must reflect the appropriate biological time scales for each pollutant and for combinations.

5.2.1.3 Evaluation of Health Outcomes

Many health outcomes have been associated statistically with air pollution, and the spectrum of potential effects continues to increase as relationships between exposure and additional health outcomes and biomarkers are examined. Health outcome data are sometimes collected specifically for an individual study, but due to the cost of measuring detailed health data directly, such studies are typically limited to measurement of symptoms or physiological parameters in small populations. Most contemporary epidemiological studies make use of health data that are collected for other purposes.

Limitations of Administrative Data. Administrative data can be defined broadly as those which are collected routinely, usually by government agencies, for purposes other than that for which they are being used in a given analysis. In air pollution epidemiology, the most frequent example is mortality data, which are routinely collected from death certificates as part of vital statistics systems in many countries. Other examples include data pertaining to hospital admissions and visits to emergency departments or physicians, which might be collected for the purpose of financial management of health services. The obvious advantage of these data is that there is no incremental cost for data collection because they are being collected anyway. However, the fact that they are originally collected for other purposes means that information which might be particularly relevant to a given hypothesis about air pollution is often lacking (e.g. information on smoking or occupation). Another issue is the accuracy of diagnosis; death certificate data in particular are known to be inaccurate, especially for some types of conditions. Although the analysis of administrative data to examine the health effects of air pollution generally only involves the use of aggregate data in which specific individuals are not identified, increasing attention to protection of personal privacy is presenting new obstacles to accessing the data and linking them to personal exposure.

Variation Among Countries. In Canada, mortality data are routinely available, although in recent years there has been an increasing delay between date of death and availability of mortality data, due in some cases to budget cuts affecting registry offices. While Canada's universal public health care system theoretically provides an opportunity to uniformly capture health service utilization data for hospital admissions, emergency department visits and physician office visits, in practice these data have been neither consistently or readily available to researchers. Because health care falls under the jurisdiction of provinces, data collection procedures are not always uniform across the country.

In Mexico, the National Institute of Geography and Statistics (INEGI) is in charge of publishing official information concerning mortality at a national level. The original information is extracted from death certificates and includes socio-demographic data (except for infants and children) as well as the primary cause of death. Death certificates are coded manually and captured in an electronic system with a built-in consistency check by trained personnel. Validity of coding and information provided on the death certificate is checked regularly (www.inegi.gob.mx). Causes of death and morbidity data are classified using the International Classification of Diseases (currently the tenth revision, ICD10). In contrast, data for emergency visits and hospital admissions are not systematically recorded and the information is kept for only short times. However, the Instituto Mexicano del Seguro Social (IMSS) is currently storing morbidity data electronically, which should provide a large data basis. Access to these data, however, will depend on the willingness of the IMSS to share these data and on patient privacy issues.

In the United States, mortality data are collected by the states and submitted to a federal agency (National Center for Health Statistics), which summarizes them and classifies them with respect to cause of death. In recent years, concerns about privacy have made access to these data difficult. Access is still possible, but the difficulties have led many researchers to obtain data directly from the states when possible. Hospital admission data vary considerably from hospital to hospital in the United States. Generally, permission for access to records must be obtained from each hospital individually. In some cases, state hospital organizations collect the data, and these may be available to researchers. Hospital data for the population over 65 can be obtained from federal Medicare records; zip code and disease classification data are generally available from this source as well. Other health data sources are limited and haphazard. Data on physician visits can sometimes be obtained from health maintenance organizations, as can data on patients with implanted cardioverter defibrillator devices. Again however, access to these data is limited, and patient privacy issues limit both the amount and detail of information that can be obtained from these sources.

Disentangling the Roles of Different Pollutants and Combinations of Pollutants. Movement toward multipollutant air quality management increases the need to relate health outcomes to multiple pollution variables, in order to distinguish the effects of individual pollutants and combinations. The consideration of many different pollutants and their interactions can create a statistical problem (multiple comparisons), which increases the likelihood of finding false positives. One way to limit this would be to test a small set of hypotheses about specific associations specified in advance. Other pollutants and combinations thereof should be considered in secondary analyses, to inform the science for developing future hypotheses. The consideration of multiple pollutants with the goal of determining their relative causality is complicated. The greatest statistical power comes from comparisons providing strong contrasts in the relative proportions of the different pollutants in the mixture. Because many pollutants come from the same sources, their ambient concentrations are often correlated. Meteorological considerations are another complicating factor; the same conditions that produce high levels of one pollutant are also likely to produce high concentrations of other pollutants. The difficulty of disentangling the effects of different pollutants on health is complicated further by the fact that estimates of individual exposures to various pollutants are subject to different levels of measurement error, and this can influence estimates of the association between a given pollutant and a health outcome.

Because concentrations of ambient pollutants used to represent exposures in epidemiological studies are often correlated, one pollutant can confound the observed relationships of others with health outcomes. As a result, in attempting to quantify the broad public health impact of the mix of pollutants, as was done in the case of the Global Burden of Disease analysis (Ezzati et al. 2002) or as carried out in estimating the benefits of air quality management programs, a single pollutant (often PM) or in some cases two pollutants (often PM and ozone) are chosen to conservatively avoid the "double counting" of impacts among multiple correlated pollutants. This probably underestimates the true impact of the mix of pollutants, just as simply summing effects over multiple pollutants unadjusted for concurrent effects of co-pollutants is likely to overestimate it. At the same time, the effects of one pollutant could modify the impact of others (i.e., the impact of pollutant A is higher or lower as the concentration of pollutant B increases—an example of "effect modification"). This phenomenon is rarely examined in epidemiological studies of air pollution. Thus, in order to accurately quantify the impacts of multipollutant management, it will be necessary to both improve the capacity to account for confounding among pollutants (the degree of additivity), as well as effect modification (the degree to which their effects are modified in the presence of another pollutant).

Given the above potential complications, there are several caveats that must be placed upon the estimated associations between health outcomes and specific pollutants—even when only considering single-pollutant effects. Considering more than one pollutant in a model is one way that can help inform the role that one pollutant may have relative to others. Other approaches include the consideration of toxicological and exposure data, which can help inform the weights given to the associations between health outcomes and different pollution variables in a given study. For example, a study conducted indoors that found an association between ozone and a health outcome would be greeted with skepticism, because indoor exposures of ozone are typically so low in relation to outdoor levels. Compounds such as the reaction products of ozone and organic gases could be considered more likely causal agents, because of their relationship with ozone and because toxicological studies demonstrate their toxicity.

Statistical methods such as principal components or factor analyses can be used to group pollutants. The resulting groups are statistically independent and include, within a group, pollution measures that are highly correlated. These groups can be used as pollution indices, which can be considered in models to assess their association with health outcomes. Pollutants may be grouped by chemical class, source, or atmospheric process. For example, Mar et al. (2000) considered the relationship between both specific pollutants and groups of pollutants and daily mortality. Factors consisting of groups of pollutants may not identify the specific pollutant causing the health outcome, but they can help narrow the focus of attention to a limited set of pollutants of concern. Terminology for multivariate factors must be chosen cautiously, and especially terms that denote sources. It may be found that a single component within the factor that drives the health effect has multiple sources. Moreover, source signatures can change over time, and the treatment of secondary pollutants can be problematic in these taxonomies.

5.2.1.4 Laboratory Studies

Laboratory studies play important roles in our understanding of pollution-related health risks. Laboratory studies have typically measured the effects of specific pollutant species generated in the laboratory (e.g., ozone, Bosson et al. 2007) or effects of materials collected in the environment and administered in the laboratory (e.g., ambient PM, Seagrave et al. 2006). In addition, it has become more common over the past decade to expose animals or humans directly to ambient atmospheres drawn into stationary or mobile laboratories either unchanged (e.g., on-road aerosols, Elder et al. 2007) or after concentration of a pollutant class (e.g., concentrated PM, Sun et al. 2005).

Advantages and Limitations. The advantages and limitations of laboratory research are complementary to those of epidemiology. Experimental exposures of humans (Utell and Frampton 2000), animals (Kodavanti and Costa 2001), cells (Devlin et al. 2005) and non-cellular systems (Li et al. 2003) have three chief advantages. First, the exposure term is well-known because most laboratory exposures can be planned, controlled, and characterized in great detail (e.g., combustion emissions, McDonald et al. 2006). Exposures to single pollutants or complex source emissions (Bosson et al. 2007) or to synthetic combinations of pollutants (Laumbach et al. 2005) can occur at a time and place, and for a length, of the investigator’s choosing.

Second, biological responses to exposure can be measured in more detail and with greater precision than is typical of most epidemiological studies. Measurements such as segmental airway lavage, peripheral vascular reperfusion rates, and real-time electrocardiography can be performed on humans. Both those measurements and a much broader range of invasive and terminal procedures can be performed on animals. Importantly, the measurements can be performed at known times relative to exposure. Some measurements can be performed during exposure, and others can be performed serially if they are non-invasive or if serial sacrifice groups are included in the experimental design.

Third, the subjects can be selected to target specific human subpopulations or biological responses. Experimental exposures of humans have included the elderly, (Gong et al. 2005), asthmatics (Koren 1995), and subjects with other pre-existing diseases (Gong et al. 2005). Animal “models” of human conditions can be selected from many species, strains, ages, and genders (Kodavanti and Costa 2001; Mauderly 2000), and the portfolio of animals having genetically-engineered susceptibilities increases continuously (e.g., atherosclerosis, Sun et al. 2005). Specific tissues, such as freshly excised lung slices or vessels, can be exposed directly in vitro to airborne pollutants (Bion et al. 2002) or to collected portions of pollution mixtures (Campen et al. 2005). Both "primary" cells (collected from subjects, e.g., Seagrave et al. 2007) and standardized "cell lines" (available commercially, e.g., Sharma et al. 2007) are commonly used.

Laboratory studies also provide advantages for developing biomarkers of exposure and effects, and for determining the biological pathways linking exposures to effects. Although biomarkers and response pathways identified in animals must be validated by confirmation in humans, only the laboratory models allow the controlled exposures, invasive procedures, and defined genetic variables that are often necessary for this research.

A key limitation of laboratory studies is that the experimental subjects, whether human or animal, are often not the subjects of greatest interest. Both common sense and the required oversight of Institutional Review Boards (IRBs) prevent purposeful exposures of the most frail human subjects, and thus those most likely to be sensitive to the effects of pollutants. There are numerous animal models that simulate certain features of human susceptibilities, such as asthma (Barrett et al. 2006) and cardiovascular disease (Sun et al. 2005), but none fully models the complex combination of genetic, lifestyle, and clinical factors producing the most sensitive humans. Moreover, no animal is simply a small human; there are great variations in anatomy, metabolism, and susceptibilities among species and strains. In vitro cell and non-cellular test systems can provide great insight into mechanisms of toxicity, but cannot represent the integrated responses of intact subjects. These shortcomings present a challenge in extrapolating laboratory results to the population and exposure of greatest interest.

Another limitation is that laboratory studies cannot simulate the full range of activities, stresses, and confounding factors inherent in "free-living" populations. Another limitation is that the non-inhalation routes of exposure and direct exposures of cells often employed in laboratory studies introduce additional uncertainties about the relevance to responses in intact humans. Yet another limitation is that the doses applied to animals and cells are often much higher than those received by populations in the environment, and laboratory studies often fail to explore dose-response relationships down to realistic levels. High dose is not an acceptable substitute for high susceptibility or long-term exposures. Not only do many biological responses have non-linear relationships to dose, but the mechanisms of response can also be different at high and low doses. On the other hand, a lack of significant effects at a high dose provides some confidence that lower doses are not of concern. Finally, the composition of the exposures in the laboratory is typically unrealistic. This is an advantage when examining the effects of single pollutants, simple combinations, or fresh source emissions, but humans are always exposed to these agents amidst a much more complex background of pollutants.

Roles in Air Quality Management Decision-Making. Laboratory studies contribute to air quality management decision-making in important ways despite their disadvantages. Ambient air quality standards for most criteria pollutants such as

PM (EPA 2006a) have primarily relied on epidemiological evidence of exposure-risk relationships. For those pollutants, the results of experimental exposures of humans, animals, and cells have served primarily to: (1) bolster confidence in the plausibility of the epidemiological observations; (2) clarify the relative importance of different physicochemical components; (3) determine the biological mechanisms of response; (4) explore heterogeneity in dose and susceptibility; and (5) develop biomarkers of exposure and effects. Experimental exposures of humans have played a more central role in setting standards for other criteria pollutants such as ozone (EPA 2007) and CO (EPA 2000), because of the greater importance to decision-making of acute physiological responses in susceptible individuals.

Animal studies have played a key role in the identification and prioritization of many non-criteria pollutants (e.g., HAPs). These pollutants are generally controlled by emission standards that seek to eliminate effects documented in studies of carcinogenicity, developmental toxicity, neural toxicity, and other outcomes that are not as well documented in population studies (EPA 2006b). Studies of fundamental biological mechanisms (i.e., cellular and molecular response pathways) largely contribute by bolstering the plausibility of links between exposures to pollutants and observed health outcomes, and by facilitating the discovery of biomarkers of exposure and effects that are useful in experimental and epidemiological studies of humans.

Determining Contributions of Pollutants to the Effects of Mixtures. Controlled experiments conducted in the laboratory will inevitably play an important role in understanding which components of complex environmental air pollution mixtures cause which health effects and whether there are combinations of pollutants whose effects are non-additive. Parsing the effects of combinations and complex mixtures of pollutants in air and other media is a longstanding challenge, about which much has been written (NRC 1988; Mauderly 1993, 2004, 2006; Samet and Speizer 1993; ATSDR 2001). Studying every pollutant individually will not succeed; there are too many, some exist only in equilibrium with others, and effects may differ in the presence of co-pollutants. Studying all of the nearly infinite variations of pollutant mixtures is clearly impossible. We do not have the information necessary to estimate the effects of realistically complex air pollution mixtures using mathematical models based on chemical structure-function relationships, although such modeling has been useful for some chemical mixtures (Liao et al. 2002; Dennison et al. 2004).

There are only a few fundamental approaches to identifying causal components of mixtures and the importance of combinations; however, a large range of experimental designs and tools can be applied within those few general approaches. One approach is to study combinations of pollutants in a factorial study design; i.e., for pollutants A, B, and C, conduct identical studies of A, B, C, A+B, A+C, A+B+C, and a negative (and possibly positive) control exposure. This approach has been used to study the effects of two or three pollutants using experimental exposures of humans (Anderson et al. 1992) and animals (Kleinman et al. 2000), and was successful in demonstrating the relative impacts of these few pollutants. This approach is useful for testing hypotheses about specific inter-pollutant interactions, but is impractical for mixtures having numerous components. The permutations of more than three pollutants become so numerous that they are seldom practical to encompass within a single study.

A second general approach is to study more complex, but still limited, mixtures of pollutants using dissective strategies that identify the causal components. A classical example of this so-called "bio-directed fractionation" is the iterative chemical fractionation and in vitro testing used to identify components of extracts of ambient and combustion-derived PM responsible for bacterial mutagenicity (Schuetzle and Lewtas 1986). In that case, the mixture was chemically complex, but represented only a portion of the environmental exposure atmosphere. Another example of using a dissective strategy was the filtration of gasoline engine emissions to demonstrate the relative contributions of PM and non-PM components to cardiovascular effects in mice (Lund et al. 2007). A third, and currently relevant, example is the study of concentrated, size-classified, ambient PM (CAPs). Although only one pollutant class is concentrated, that component is in itself complex and study designs using multiple exposures can point toward causal components (Wellenius et al. 2003). In the preceding examples, portions of mixtures were sequentially subtracted or isolated to identify causal components, but the same conceptual approach could involve "doping" the sample or exposure atmosphere to markedly increase the concentration of a component.

A third general approach involves multivariate analysis of data from identically-designed studies of multiple mixtures having contrasting composition. If enough mixtures are studied, if the compositions of the mixtures overlap but differ sufficiently, and if the effects differ sufficiently among mixtures, multivariate statistical methods can determine which components co-vary most strongly with the effects. An example of this approach is the identification of engine oil components as potential contributors to the lung inflammatory potential of mixtures of PM and semi-volatile organics collected from vehicle emissions (McDonald et al. 2004). Another example is the linkage of components of PM from Mexico City to biological activity (Rosas-Pérez et al. 2007). This approach is a good way to generate hypotheses, but follow-up studies are typically necessary to confirm that the components co-varying with effects are indeed the causal species.

Importance of Systematic Comparative Research. In view of the staggering breadth of pollutants, health issues, and potential research approaches, attention should be given to developing high-level systematic research strategies. The diversity of interests, hypotheses, research tools, and funding incentives among the research community facilitates a wide-ranging exploration of cause-effect relationships and biological mechanisms. However, these factors can work against developing a cohesive understanding of the relative impacts of different air pollutants (Mauderly 2004; NRC 2004). It is exactly such a cohesive, integrated understanding of the relative importance of different pollutants that is needed to inform multi-pollutant air quality management. The large range of pollutant classes, compounds, combinations, and health outcomes can only be encompassed by studies conducted by multiple groups and funded by multiple sponsors. Without high-level attention to establishing a multi-dimensional matrix of pollutants, sources, health outcomes, and health response models, and without using that matrix to allocate research resources, multipollutant health research could produce an assortment of findings that does not provide a systematic comparison of the relative effects and potencies of different pollutants. For example, the National Research Council (NRC 2004) identified an insufficiently systematic approach as having retarded progress toward understanding the relative importance of different components of PM.

The matrix of information gaps pertaining to multipollutant health research is highly multi-dimensional. One dimension of a strategic research matrix is ensuring the evaluation of the full spectrum, or at least a prioritized range, of pollutant classes and combinations. Without attention, some pollutants will inevitably be studied intensively and others will be ignored. Another dimension is ensuring consideration of the full spectrum, or a prioritized subset, of the known or suspected health outcomes. Another dimension is ensuring that each pollutant class is evaluated for its potential to cause multiple health outcomes. Finding that a pollutant has a certain effect (e.g., lung inflammation) is useful, but it is even more useful to know whether that component also causes other effects (e.g., cardiac arrhythmia, amplification of allergic responses, DNA adduction, etc.). Yet another dimension is considering the comparability of results from different biological response models. It is useful to confirm biological activity in more than one model before drawing conclusions having significant societal ramifications. Sometimes information from multiple assays is concurrent, such as the similar inflammatory potential of ambient PM samples from the Utah Valley in humans, animals, and cells (Ghio 2004). However, different assays sometimes yield conflicting results, such as the nearly opposite rankings of the toxicity of the same engine emission samples in animals and cells (Seagrave et al. 2005).

Within the bounds of plausible resources, it is probably impossible, and likely unnecessary, to fill every potential "cell" in the multi-dimensional research matrix. This makes it all the more important for multi-sponsor research strategies to be prioritized within the framework of such a matrix, to ensure the pollutant classes and health outcomes thought most important are addressed in a systematic, goal-driven manner.

5.2.1.5 Linkages Between Epidemiology and Toxicology

A call for improved linkages between epidemiological and toxicological research results from most discussions of research strategy, motivated by the uncertainties involved in extrapolating findings and conclusions from one to the other. Just what "linkage" could mean and how to accomplish it have been challenging to define. It is certain that a cohesive multipollutant research plan will employ the complementary strengths of both population and laboratory studies. How they might be combined into a truly integrated strategy and when it is appropriate to do so are less clear. A truly integrated, parallel approach would require commonality of exposure atmospheres and measures of outcomes.

Loose linkages between epidemiology and laboratory studies most commonly occur as independent studies aimed at a common issue, as exemplified by the huge, diverse body of research on PM (EPA 2004a). Information gaps and research needs are "handed off" from one research community to the other either informally as results and questions are made known through presentations and publications, or formally and more rapidly within multidisciplinary research centers (e.g., the EPA PM research centers). Research on the impacts of ozone on lung development and growth presents an example of this type of multidisciplinary research. Epidemiological evidence that chronic exposures lead to reduced lung function of college students (Tager et al. 2005) was supported by the finding by a toxicological research group that repeated exposures of infant monkeys can alter airway development (Fanucchi et al. 2006).

Three basic approaches are used to more closely integrate epidemiological and laboratory research tools to resolve exposure-response relationships: (1) expose "laboratory models" to the same atmosphere as encountered by the population studied by epidemiology; (2) expose laboratory models to materials collected from locations of target population exposures and brought to the laboratory; and (3) expose laboratory models to atmospheres generated in the laboratory to simulate pollutants and mixtures to which target populations are exposed. Although animals exposed to actual ambient atmospheres have demonstrated pollutant-related effects (e.g., Soares et al. 2003), there has been little attempt to conduct exposures in places and over times coordinated directly with epidemiological studies. The exposure of humans or animals to concentrated PM in areas of epidemiological study (e.g., HEI 2007a; Lippmann et al. 2007) resembles this approach, although only one pollutant class is concentrated and the spatial-temporal relationship to population exposures is uncertain. An example of the second approach is the experimental exposure of humans, animals, and cells to PM collected in the Utah Valley during an epidemiological study, resulting in coherent evidence for causal composition-response relationships (summarized in Ghio et al. 2004). Although many laboratory exposures to single pollutants or mixtures target health effects that are also suggested by epidemiology, few programs have involved proactive coordination of the population and laboratory studies. Perhaps the closest example is the current program involving the concurrent study of cardiovascular outcomes among women in regions having different pollution mixtures and predominant sources, and exposures of animals to atmospheres simulating key contrasts among the population exposures (HEI 2007a; Vedal et al. 2007).

5.2.2 Current Understanding of the Impact of Air Pollution on Health

5.2.2.1 Confidence That Health Is Impacted by Air Quality

Observations of Pollution-Health Relationships. There is no doubt that increases in air pollutant concentrations can have adverse effects on health. This has been vividly demonstrated by several historical air pollution episodes in the last century in which dramatic increases in concentrations resulted in abrupt increases in deaths (Holgate et al. 1999). While observations based on these episodes are convincing in demonstrating that air pollution can cause serious adverse health effects, they do not provide much help in determining whether exposures to the much lower ambient concentrations currently measured in North America and elsewhere also have adverse effects on health.

The evidence that exposures to these much lower concentrations also have adverse effects on health is largely observational in nature. Confidence in observational findings, in this context, is primarily a function of our confidence that confounding is not responsible for estimated associations between increased air pollutant concentrations and ill health. In other words, we must have sufficient certainty that these associations are not merely spurious associations. Other considerations that influence our level of confidence in these studies include the role of exposure measurement error, statistical model misspecification and publication bias. Gauging the impact of publication bias, due both to investigators being selective about the results they choose to report and to the tendency of journals to publish findings that indicate effects, is difficult. In the context of ozone, at least, the impact of publication bias on epidemiological estimates of effect has been found to be substantial (Bell et al. 2005). Although confounding and these other factors are all operative, none has been found to be responsible for producing the reported observational associations between increased air pollutant concentrations and ill health (Samet et al. 2000b).

"Natural Experiments." One type of observational study that has been especially valuable in increasing our confidence in current air pollution health impacts is the quasi-experimental study in which population health effects are studied in relation to a relatively sudden and dramatic change in air pollution concentrations as a result of either an intentional action to change concentrations or an action that indirectly reduces concentrations (the so-called "natural experiment"). Examples of the former type are rapid institution of air pollution control policies such as a ban on residential coal burning (Clancy et al. 2002), or mandating reduction in the sulfur content of fuel (Hedley et al. 2002). Examples of natural experiments are industrial labor strikes that reduce industrial emissions (Ransom and Pope 1995), a change in traffic density associated with the Olympic Games in Atlanta (Friedman et al. 2001), or rapid modernization resulting in much lower industrial emissions such as occurred with German reunification (Heinrich et al. 2000). Because none of these studies was strictly experimental and the "intervention" also caused changes in factors other than air pollution concentrations, the interpretation of findings from these studies is not always clear. Nevertheless, our confidence in air pollution effects has been enhanced by the findings of these studies.

Toxicological Evidence. Toxicology has played a critical role in enhancing our confidence in the observational findings. Demonstrating effects of air pollutants in animal experimental studies and in vitro studies has increased the plausibility of the observational findings and provided insight into possible mechanisms of air pollution effect. The recent demonstration of worsened atherosclerosis in a susceptible mouse model exposed to concentrated ambient particles has been particularly influential in this regard (Sun et al. 2005); although, the relevance to humans of findings based on animal and other experimental models can always be questioned. Human experimental studies have therefore also played an important role in enhancing plausibility and in gaining insight into mechanisms. Human experimental studies, because of constraints in studying the potentially most susceptible subjects and in exposing them for an extended period of time, may not give a full picture of the scope of air pollution health effects in the population.

5.2.2.2 Scope of Health Outcomes Impacted

The range of health effects attributed to air pollution exposure has expanded dramatically in recent years. The initial focus was primarily on respiratory outcomes. Largely because of the observed effects of air pollution on total mortality, it was clear that effects on organ systems other than the respiratory system must also be occurring, most notably effects on the cardiovascular system. Findings from observational, human experimental and toxicological studies have now combined in indicating that a range of cardiovascular effects of air pollution exposure can occur (Brook et al. 2004). Effects on atherosclerosis may manifest themselves in a host of clinical diagnoses including myocardial infarction, congestive heart failure and cerebrovascular events, all of which have been associated with short-term increases in PM concentrations in observational time series studies and in cohort studies (Pope and Dockery 2006). Effects of PM exposure on measures of cardiac autonomic tone have been reported in multiple observational studies (Adar et al. 2007; Pope et al. 1999; Gold et al. 2000; Luttmann-Gibson et al. 2006) and in some human experimental studies (Samet et al. 2007).

Ambient air unquestionably contains many known carcinogens and mutagens in both the particulate and non-particulate phases, which makes a contribution of pollution to the burden of cancer at least plausible (Claxton and Woodall 2007). Until recently, the observational evidence that low level environmental exposure to air pollution caused lung cancer was based on relatively weak evidence, such as that provided by ecologic studies. Ecologic studies, in which data on exposure and cancer are aggregated at the group level rather than at the level of individuals, are prone to biases that make them difficult to interpret. The American Cancer Society cohort study used individual-level data on cancer diagnosis and cancer risk factors such as cigarette smoking, and as a result has provided the most convincing evidence of an effect of PM on increasing risk of lung cancer (Pope et al. 2002). The cancer risk among the general population from air pollution most likely results from many years (perhaps a lifetime) of exposure. This latency of effect complicates evaluating associations with air pollution, especially when air pollution data are available for only a small portion of the exposure period.

We currently have less confidence in air pollution effects on organ systems other than the respiratory and cardiovascular systems, although there is some evidence for this. Effects of PM on birth outcomes especially, including premature birth and low birth weight, have been reported now in several observational longitudinal and cross-sectional studies (Sram et al. 2005). While these studies still present problems in attributing the associations as causal, their findings are concerning. Some have suggested that PM also has effects on the nervous system, and might increase risk of Alzheimer's disease, for example (Calderón-Garcidueñas et al. 2004). Further studies are clearly needed to move these initial observations beyond the hypothesis generation stage.

5.2.2.3 Uncertainties in Attributing Risks to Specific Pollutants and Sources

Criteria Pollutants. PM has received the most recent attention in observational and experimental studies. Effects of both short-term and long-term exposures to PM in observational studies have generally been shown not to be due to other pollutants with which PM is often highly correlated, at least those pollutants whose concentrations are measured (Pope and Dockery 2006), although there have been some specific exceptions (Moolgavkar 2000). Although many pollutants were not measured in epidemiological studies, the experimental effects of PM have arguably provided the most compelling evidence that exposure to PM itself causes adverse effects (Brook et al. 2002; Sun et al. 2005). There is controversy as to which features of PM are most critical to its toxicity. Possibilities include PM chemical composition, physical features such as size, number or mass, and other features such as pH, solubility or redox potential.

Ozone has long been known to cause adverse effects, shown most convincingly in the human experimental setting with respect to level of lung function and airways inflammation (Lippmann 1989). The observational evidence relating to ozone implicates either ozone itself, or the photochemical oxidants that are part of the photochemical pollutant mix, in many of the same health outcomes as has been observed for PM. Because effects of ozone on level of lung function in children in non-experimental settings are typically larger than those seen in exposure chambers, it is not unreasonable to assume that some components in the photochemical mix, of which ozone is just a part, are responsible for the enhanced effect (Spektor et al. 1988; Romieu and Barraza 2007). It is difficult to believe that the associations between short-term changes in ozone at very low concentrations and daily mortality (Bell et al. 2004; Gryparis et al. 2004) are due to specifically to ozone, largely because those at risk of death in time series studies, namely the ill elderly who spend most of their time indoors, have very little exposure to ozone. However, it is likely that the changes in outdoor ozone concentrations result in formation of indoor ozone reaction products that themselves might be responsible for causing death in susceptible individuals (Weschler 2006).

Of the criteria air pollutants other than PM and ozone, nitrogen dioxide (NO_2) has been shown to be most consistently associated in observational studies with the severe array of health outcomes observed for PM and ozone (Samoli et al. 2006). Based on the experimental findings of NO_2 exposure which do not indicate much potential for the ill effects suggested in observational studies, it is likely that these "effects" are either spurious or reflect the role of NO_2 concentrations as a surrogate measure of other pollutants that could cause such effects. Determining whether measures of pollutants such as NO_2 are simply acting as surrogate measures of more toxic pollutants is complicated. It is likely that the more toxic pollutants that NO_2 concentrations might reflect would be expected to differ over both time and space, and to be different in the short-term and long-term exposure settings. The experimental data base on cardiovascular effects of both ozone (Gong et al. 1998) and NO_2 is admittedly small relative to that for PM. Knowledge of the potential cardiovascular effects of these pollutants is therefore only limited at this point; better understanding of these effects could conceivably result in a reconsideration of their roles in producing the epidemiological associations. Studies of exposure to indoor levels of NO_x could be helpful in understanding the role of NO_x in health responses.

Higher ambient sulfur dioxide concentrations have been associated with increased mortality in observational studies of long-term exposure effects (Pope et al. 2002). In one quasi-experimental study, a reduction in respiratory mortality was observed following dramatic reduction in SO_2 concentrations (Hedley et al. 2002). While this effect on mortality was not due to a lowering of PM concentrations, other pollutant concentrations, such as nickel and vanadium fell in concert with SO_2 (Chen and Lippmann 2009). In addition, no plausible mechanism has been proposed whereby SO_2 at these concentrations could produce such effects.

Human exposure studies have provided strong evidence that concentrations of CO that may be experienced in environmental settings can be harmful, particularly in individuals with ischemic heart disease (Allred et al. 1989).

Source Emissions. Partly because of the obvious implications for air pollution control, there has recently been great interest in investigating effects related to emissions of specific air pollution sources rather than to concentrations of individual air pollutants (Hopke et al. 2006). Much of the focus has been on traffic emissions. Observational studies have used indirect measures of exposure to traffic, such as distance to major roadway or traffic intensity within a given radius of the place of residence. These have generally shown associations with both respiratory and cardiovascular outcomes (Hoek et al. 2002; Gauderman et al. 2007). These exposure measures are not specific for traffic-related air pollutants and could reflect other traffic-related exposures such as noise. In at least one study, however, investigators have attempted to separately control for effects of noise and the associations with traffic remained (Brunekreef—personal communication 2007). Other stresses associated with traffic have received little attention. Controlled human exposure studies have identified cardiovascular effects of diesel exhaust exposure and an effect of diesel exhaust in enhancing allergic reactions (Diaz-Sanchez et al. 1994). Whether these effects are specific to diesel emissions as opposed to other vehicular and combustion emissions is not clear. There is a substantial literature showing that exposures of animals to high concentrations of diesel emissions can cause a spectrum of respiratory, cardiovascular, and developmental effects (Mauderly and Garshick 2009), but there have been few direct comparisons with effects of other source emissions.

5.2.2.4 Exposure-Response Functions

The slope of exposure-response functions for air pollutants is directly related to the size of the estimates of effect generated by epidemiological studies. Uncertainties in estimation of effects, then, due to factors touched on above (see "Observations of pollution-health relationships"), translate into uncertainties in the exposure-response function. Concern over uncertainties in epidemiological effect estimates was heightened following the recent discovery of the improper application of statistical analysis software used in analysis of time series data (Dominici et al. 2002; Lumley and Sheppard 2003). In general, the end result of correcting this problem was a reduction in the size of effect estimates and thereby a flattening of the slope of the exposure-response function.

In the large majority of population studies in which an attempt has been made to assess the exposure-response function relating air pollution exposure and health effects, investigators have been unable to confidently determine that there are concentrations below which no effects are observed to occur. This has been best studied in the case of PM (Daniels et al. 2000). Similar conclusions have been reached in the many fewer similar studies on ozone (Gryparis et al. 2004; Bell et al. 2006). In the case of ozone, based on human and experimental studies, there was a general understanding that effects were not produced at very low concentrations (Horstman et al. 1990; Adams 2006). At least for daily mortality, however, observational studies surprisingly show effects of ozone at these low concentrations (Gryparis et al. 2004; Bell et al. 2006). While exposure measurement error would be expected to be much greater for ozone than PM, and could obscure a threshold in the exposure-response function (Brauer et al. 2002), limiting the study to only days with very low ozone concentrations does not result in changes in the effect estimate, indicating that effects do indeed persist at low concentrations (Bell et al. 2006). Studies done in cities with very low PM and ozone concentrations also show pollutant effects (Vedal et al. 2003). As noted above, at least for the case of ozone, while attributing low concentration effects to ozone itself does not seem plausible at this time, ozone concentrations in these settings likely serve as a measure of concentrations of a complex mix of oxidant pollutants which could conceivably be responsible for low-concentration effects.

5.2.2.5 Synergisms Among Pollutants

There is longstanding concern that combinations of pollutants might have greater than additive effects, and the literature contains several reviews and strategies for the risk assessment approaches for mixtures (ATSDR 2001; EPA 2000a; NRC 1988). Our understanding of synergistic interactions in which simultaneous or serial exposures to more than one pollutant have greater than additive effects is limited. There is little direct epidemiological evidence for differential effects of combinations of individual pollutants beyond those attributed to the individual pollutants alone. However, epidemiological studies have little power to assess differential effects of pollutant combinations. The real-world oxidant pollution scenarios noted above in Sect. 5.2.2.3, Criteria Pollutants (Spektor et al. 1988) may reflect enhanced effects of a combination of photochemical oxidant pollutants beyond the effect of ozone alone, but there may also be other explanations for the enhanced effects in these settings. Experimental exposures of humans and animals have produced several examples of synergism between air pollutants, although combined effects have been more often additive or sub-additive than synergistic (Mauderly and Samet 2009).

5.2.2.6 Effects of Air Pollution vs. Other Causes

Determining the magnitude of air pollution health impacts has by necessity relied on findings of observational studies (Künzli et al. 2000) and, to a lesser extent, the subset of quasi-experimental observational studies referred to above (see "Natural Experiments"). The pollution effects found in quasi-experimental studies have been at least as large as those from other observational studies, and often larger (Clancy et al. 2002). The unavoidable reliance on effect estimates from observational studies makes the task of assessing population impacts subject to similar uncertainties. Further, in making impact assessments, one implicitly assumes that the response to pollution exposure in populations used in generating effect estimates is reasonably comparable to that of the population for which impacts are estimated.

The Global Burden of Disease initiative and others have attempted to estimate relative impacts of known disease risk factors internationally, using observational effect estimates (Lopez et al. 2006). The contribution of air pollution in any given disease obviously depends on the disease of interest, and also on whether air pollution influences the effect of other disease risk factors. Ambient air pollution worldwide has been estimated to cause 3% of cardiopulmonary deaths, 5% of lung cancer deaths, and 1% of deaths in children less than age 5 from acute respiratory infections (Cohen et al. 2005). Others have estimated air pollution to cause only 2% of lung cancer in nonsmokers (American Cancer Society 2006), the subset of the population in which the estimated effect of air pollution on lung cancer is largest (Pope et al. 2002). Obviously, there remains a great deal of uncertainty in these estimates.

5.2.3 Impact of Regulatory Cycle-Driven Research on the Ability to Address Multipollutant Air Quality Management Information Needs

The majority of air pollution health research is funded through programs aimed at single pollutants or sources in response to regulatory cycles. Much more research is aimed at criteria pollutants than at other pollutant species. During the past decade for example, the resources directed at PM have undoubtedly exceeded those directed at all other pollutants combined. This is a natural reflection of a predominantly single-pollutant, single-source regulatory structure. Not only is the allocation of resources biased by contemporary regulatory issues, but experimental designs and interpretations of findings are also inevitably biased toward demonstrating and understanding effects of the pollutant of the day. Although many studies focused primarily on a single pollutant include measurements of at least a few other pollutants, the emphasis is typically more on the confounding by "co-pollutants" of the effect of the pollutant of main concern than on clarifying the relative roles of the different species.

The further the progression toward a truly integrative multipollutant air quality management structure, the more important it will become to develop a more comprehensive multipollutant knowledge base. Much good research has been done in the quest to clarify effects of single pollutants and sources, and improvements in air quality and reductions of health burdens have resulted. However, the resulting knowledge base does not serve well to reveal which of the broader spectrum of pollutants cause which health effects, their relative contributions to effects caused by multiple pollutants, or the importance of non-additive combinations. Many pollutants have received scant attention and complex mixtures have only infrequently been studied using experimental designs that disentangle composition-response relationships.

A shift in research emphasis must necessarily be driven by the providers of research funding, and this will require a change in the perspectives of government agencies. Researchers can advise on research needs and strategies, but they must ultimately react to the competitive solicitations and other funding opportunities that are offered to them. The major responsibility for shaping the general nature of the research lies with those developing the solicitations, and in turn, with those providing funding for the solicitations. The availability of data is also strongly influenced by federal decision-makers. Regulators determine air quality monitoring strategies. Governments ultimately determine the collection and availability of "administrative" health data. The greatest conceptual challenge will be for agencies to shift from funding research overwhelmingly in support of existing regulatory structures to directing a large portion of funding to forward-looking research whose impacts on future air quality management strategies cannot be predicted in advance.

5.3 Accountability in a Multipollutant Air Quality Management Context

5.3.1 Tutorial on Accountability Science

Definition and Roles. In its 2003 monograph (HEI 2003), the Health Effects Institute defined accountability as part of, "…a broad effort to assess the performance of… environmental regulatory policies". This is basically the definition we use, as noted in Chap. 3. Applied specifically to the area of air quality, this involves determining whether policies have actually resulted in the anticipated improvements in public health. The science of accountability involves utilizing tools from other disciplines including exposure assessment, epidemiology and biostatistics.

Tools. The same tools that are used to assess the health effects of pollution can be adapted to assess the benefits of specific air pollution policies. In general, however, these analyses must be considered for at least two different periods of time, the period before policy implementation and the period afterwards, at a time when the policy can reasonably be expected to have affected air quality and health outcomes. This is complicated by the fact that policies are often gradually implemented over an extended period of time and other factors that influence health (e.g., health care practices, socioeconomic factors) change over time as well. Hence, we are often confronted with the need to consider changes over a longer period of time than is generally considered in studies that are designed to assess the health effects of pollution per se. The biggest difference between accountability studies and times series studies is that the former are generally undertaken over a longer period of time during which many more intervening factors can influence the results. In addition, accountability studies are concerned health responses to longer term changes in pollution levels rather than responses to changes from day to day.

Motivations, Uses, Strategies and Successes to Date. The primary motivation for evaluating accountability is to be able to guide air quality policies based on evidence of their effectiveness, and secondarily to demonstrate that investments to improve air quality have been warranted based on benefits to public health. There are numerous challenges in attempting to document improvements in public health as a consequence of air quality policies. These primarily relate to factors which confound or obscure the causal pathway between introduction of a regulation or policy to changes in emissions, exposure and dose, and finally health status. These factors include potential impacts of the policy on personal behavior or economic activity which could also affect health, changes over the same time scale as the regulation in factors which also affect the health outcomes of interest, incomplete or delayed implementation of a regulation or policy, or a long the time delay between changes in exposure and changes in the frequency of effects. To this point, conventional health surveillance, even specifically directed at environmental health such as the Environmental Public Health Indicators Project at the United States CDC (http://www.cdc.gov/nceh/indicators/summary.htm) cannot readily identify specific health outcomes which can be tracked directly over time to provide a measure of health effects attributable to air pollution, with the exception of lead poisoning and CO poisoning.

Despite these challenges, several approaches have nonetheless been advanced to attempt to measure health benefits from improvements in air quality. The HEI document provides a review on the state of the art in this area as of 2003, and this has not changed significantly to date. Briefly, a key element of any attempt to measure health benefits involves anticipating situations where changes in air quality are expected and being prepared to measure them. Potential methodologies include serial personal exposure studies incorporated within existing nationally representative serial surveys such as NHANES; serial time series studies to assess changes in risk over time (Burnett et al. 2005); serial cross sectional studies of health outcomes of interest (potentially using existing survey data as from NHIS or NHANES); further analyses of existing cohort studies to examine effects of exposure during successive time windows of exposure; and randomized studies of interventions at the individual level (e.g., changes in time-activity or use of home ventilation/air filtration). Application of particular statistical approaches such as Bayesian analysis and causal analysis may also be informative.

Although it does not deal at length with issues related to multipollutant management, the HEI report acknowledges that, "The air pollution mixture complicates interpretation of patterns of changes in health outcomes observed after an intervention aimed at reducing ambient pollution levels". A related point is made, that source apportionment studies involving multivariate statistical techniques can be used to try to identify specific source signatures responsible for adverse health effects. Although consideration of sources may be useful for framing multipollutant management approaches, the fact that many pollutants and their precursors have multiple sources severely limits the utility of source terms as exposure terms for allocating causality of health effects.

The most persuasive evidence to date demonstrating the effectiveness of air quality policies consists of a small number of studies conducted in relation to "natural experiments", where rather dramatic improvements in air quality and accompanying reductions of health burdens have occurred over a short time, reducing the potential impact of confounding factors (Clancy et al. 2002; Hedley et al. 2002; Pope et al. 2007; Pope 1989).

5.3.2 Issues and Challenges in Assessing Benefits from Air Quality Improvements

5.3.2.1 Knowledge of Exposure

Spatial and Temporal Variability. As noted earlier, human contact with pollutants may occur in various microenvironments, such as indoors at home, outdoors during commuting or walking, etc. Our current understanding of how the composition and concentrations of ambient pollutant mixtures vary spatially and temporally in urban airsheds is limited, and knowledge for rural microenvironments is even more limited. For example, near-roadway concentrations of PM species and gases can be highly variable depending on proximity to road, traffic volume, topography and meteorology. Consequently, residences, offices or schools located near busy roads may have higher concentrations of ambient pollutants infiltrating indoors. Source-specific contributions to personal exposures to PM, gases and other toxic air pollutants may vary significantly by location (e.g., ambient outdoors, indoors, commuting, etc.), by season and type of microenvironment (McKone et al. 2007). Moreover, diurnal or temporal variability in the contributions from different sources of PM and air toxics not only influence the composition of air pollution mixture in various microenvironments but also their relative toxicity to humans (McKone et al. 2007). Modeling analysis has shown that the variation in the relationships between hazardous air pollutant exposures to corresponding ambient concentrations can be highly pollutant, site and activity dependent (Özkaynak et al. 2007). Thus, the complexity in the spatial variation of exposures among the different population cohorts, especially in the context of cross-sectional or intra-urban analysis of air pollution health effects, could be quite challenging.

Modeling Exposures. Comprehensive data on multiple pollutant measurements in key outdoor and indoor microenvironments are needed in order to be able to relate ambient air pollution monitoring data to personal or population exposures. These data are then typically used in conjunction with either geographic information system (GIS)-based land-use regression (LUR) models (English et al. 1999; Jerrett et al. 2005a; Smith et al. 2006; Marshall et al. 2007; Arain et al. 2007) for estimating concentrations of pollutants at outdoor locations of concern for human exposures. In addition to available spatially distributed data, LUR models incorporate landscape characteristics, such as proximity to roadways and other outdoor sources of air pollution near subjects' homes. Personal exposure estimates may then be produced by using available measurement data with mechanistic human exposure models. For example, the mechanistic exposure models, such as the SHEDS model (Burke et al. 2001; EPA 2004b), incorporate information on sources and concentrations of pollutants in different microenvironments with corresponding human contact data derived from available time-activity diaries.

The more refined methodologies for exposure estimation have begun to be incorporated in multipollutant health effects studies (Isakov and Özkaynak 2007; Molitor et al. 2007). However, better information on time-activity, commuting and exposure factors data are clearly needed to support these models, in order to improve the assignment of exposures during the course of future multipollutant air pollution health studies. Monitoring data generally exist only for those pollutants that are regulated and therefore required to be measured routinely. If the pollutants that impact health are not measured, surrogate pollution measures must be used to assess benefits, resulting in uncertainties associated with the benefits estimates. In addition to these exposure-related considerations, it is also important to improve our current understanding of biological cause-effect time scales, through animal and human studies involving exposures to typical levels of multipollutant concentrations. On-going studies across the United States dealing with PM and a small number of co-pollutants should help clarify gaps in knowledge and opportunities for designing future studies that would address biological cause-effect and exposure-response relationships for an increased spectrum of pollutants. At the same time, this information could also serve to provide input into accountability studies. The first step in assessing the benefits of a risk management strategy is to demonstrate changes in personal exposures associated with the strategy.

5.3.2.2 Knowledge of Health Responses

Scarcity of Individual-Level Data. Except for a few studies of panels of known individuals and cohort studies of school children, much of the health response data come from data sets collected for other purposes (e.g., death certificate data, hospital admission data) and do not allow identification of which individuals are responding to air pollution exposure. Hence, the relationship between exposure and response must be inferred from the data using standard statistical methods. The more precisely we want to know health responses to pollution, the greater the need for individual-level data for both exposure and health.

Need for More Systematic Collection and Availability of Outcome Data. It is not always easy or inexpensive to obtain health outcome data which are collected for other purposes. Privacy concerns have made availability more difficult and restricted some of the information (such as more specific information about address) that could be of value in analyses. In other cases data must be obtained from individual institutions (e.g., hospitals), where collection methods are not always consistent or even amenable for analysis. It would be particularly valuable if the health community were to define its data needs explicitly and if government agencies were to work with healthcare providers to generate systematically accessible databases suitable for air pollution-health studies. In the United States, one area where health outcome data are very limited is that associated with treatment not associated with a hospital admission. In those cases (e.g., Canadian National healthcare system) where there is governmental oversight for health treatment, the data should be organized and made accessible for appropriate analyses.

Most of the epidemiological studies undertaken to date make use of routinely collected air quality data. Most often these data are reported for the averaging times for which there are regulations; hence these averaging times are most often used in epidemiological studies. A growing number of air quality measurements are made continuously; hence many different averaging times could be considered in epidemiological studies. There is a need to consider several different timescales in a systematic fashion in order to determine the minimum exposure times to a pollutant that may lead to health outcomes. This is also an area where both epidemiological and human clinical studies could contribute to resolving this issue.

Incomplete Understanding of Susceptibility. Those with pre-existing heart and lung disease as well as the elderly, children, and those who experience increased exposure in relation to outdoor work or recreation, are widely recognized as constituting groups at heightened risk of adverse effects from air pollution. Recently, additional groups including diabetics, people with heart failure, and subjects with nutrient deficiencies (Romieu et al. 2008) have also been identified as being particularly susceptible, and increased attention to genetic influences (see below) has also begun to point to genetically predisposed groups. Other health outcomes, such as neurological outcomes, have been mentioned as possibly related to pollution exposure. Clearly the task of identifying all major susceptible groups is not completed.

Limited Availability of Biomarkers of Exposure to Air Pollutants and Resulting Effects. The field of "biomonitoring" by analyzing markers of exposure in blood, urine, hair, fat, breast milk, and saliva is developing rapidly (Paustenbach and Galbraith 2006), and should increasingly benefit studies of air pollution. Exposures to the criteria air pollutants are generally not associated with either unique effects or unique biomarkers of exposure which would be useful for tracking progress in reducing exposures to these pollutants and refining our understanding of exposure-response relationships. One exception is CO poisoning (Mott et al. 2002), in which blood carboxyhemoglobin can be directly linked to exposure. That marker, however, is less useful for detecting and classifying typical exposures to low levels of CO in the environment. Correlations have been observed between environmental exposures to ozone and bulky DNA adducts (Palli et al. 2001; Peluso et al. 2005), but adduct levels can be increased by numerous inhalation and ingestion exposures and it is not clear that an adduct specific to ozone has been identified.

There has been considerable progress in establishing biomarkers of exposure to HAPs, particularly for organic carcinogens, and correlations have been found between blood levels of chemicals and DNA and protein adducts and exposure to airborne HAPs (Sexton et al. 2005; Vineis and Husgagvel-Pursianinen 2005). These markers are very useful for characterizing total exposure to many compounds that are present in air, but most of these compounds also enter the body by other routes. The fact that there are both environmental and household sources of many HAPs complicates attribution of exposures to outdoor air pollution. The wide range of persistence (half-life) of the different markers from hours to months or years also complicates exposure assessment. Despite these challenges, the availability and utility of biomarkers of exposure to HAPs is improving and an increased use of such markers as indices of exposure in air pollution research can be expected as the HAPS receive increased attention in multipollutant studies. Studies combining markers of exposure with markers of genetic polymorphisms will become more prevalent as the field of molecular epidemiology advances (Georgiadis and Kyrtopoulos 1999). Large scale biological monitoring programs such as the National Health and Nutrition Examination Survey (NHANES) in the United States (CDC 2011) are certainly increasing the opportunity to examine linkages between environmental air quality and personal exposure.

Limitations of Comparability of Results. At present each individual investigator designs studies and selects the analytical tools to apply to his/her epidemiological study. Published studies incorporate experimental designs and tools that are scientifically acceptable to the review community. Design and analytical technique can, however, influence the reported results and interpretation of a study. For example, some studies consider and report results for several pollutants, singly and/or jointly, while other studies may consider a smaller or different set of pollutants and may not report results which attempt to adjust for the presence of other pollutants. The results obtained are clearly a function of the analytical methods used. Another example is tied to the time-series methods used to estimate the association between a health outcome and a pollutant. The estimates can vary depending upon the methods that are used to estimate them (Klemm et al. 2004). Clearly, these differences can make it difficult to directly compare results, integrate findings across studies, determine whether differences in findings were based on biology or methodology, and perform meta-analyses of multi-study data. It is unclear how this problem can be overcome. Each investigator has a right to employ his or her preferred method of analysis, and it is not desirable to squelch scientific creativity. However, it would be desirable for investigators to consider alternative methods as well, so that results can be more easily compared. Because reviewers of journal submissions cannot be expected to require this in any uniform manner, such comparisons may largely be done by special initiatives. Because of these limitations, common strategies for analyzing mortality and morbidity data have been implemented in multi-center studies such as APHEA (Air Pollution and Health: a European Approach, Atkinson et al. 2001), PAPA (Public Health and Air Pollution in Asia, http://www.healtheffects.org/international/PAPA-summary.pdf), and the ESCALA (Estudio de Salud y Contaminación del Aire in Latinoamérica, Romieu et al. 2006a) projects. Data have also been made available by some investigators to facilitate replication and further analysis (Peng et al. 2006).

Impact of Long-Term Horizon for Research Planning and Funding. Considerable progress has been made in our understanding of the health effects of air pollution; however, much remains to be learned. Effective planning and management is needed to make progress as rapidly and efficiently as may be required by an evolution toward multipollutant air quality management. This poses a significant challenge for the management of research. There needs to be a high level of sustained integration among researchers and among public and private research sponsors. At present, there is no major attempt to achieve such integration. Without it, progress is likely to be uneven and haphazard. For further discussion about this issue, see NRC (2004).

5.4 Guiding and Assessing the Effectiveness of Multipollutant Air Quality Management Strategies

5.4.1 Key Enabling Factors

The overarching key to improving the ability of the health research community to guide multipollutant air quality management and assess its effectiveness is a commitment to directing the research enterprise toward addressing the limitations and deficiencies described in preceding sections. There are technical limitations, but their importance is secondary to the need to direct efforts purposefully to fill knowledge gaps. This first requires an acknowledgement of the strengths and limitations of our current understanding of the air quality-health relationship. It next requires a conviction among the research and research sponsor communities that meeting these needs should be the primary, or at least a significant, emphasis of air pollution research. Finally, a commitment of research sponsors to focusing resources toward key needs is essential. It is important to recognize that the limitations of present knowledge and thus future research needs are not unique to multipollutant air quality management. For the most part, they simply reflect our current state of air quality health research, and moving in the directions suggested below will largely be necessary whether or not regulators intend major changes in air quality management strategies.

5.4.2 Strategies for Reducing Present Limitations

5.4.2.1 Improving Assessment of Exposure

Because direct personal measurements of exposure of all study subjects to all pollutants cannot be practically obtained, it is important to consider various alternative surrogates or indicators of multipollutant exposures. These surrogates and indicators can range from simple to complex, depending on the particulars of the assessment. A number of different surrogates of personal exposures have already been used in epidemiology studies of criteria pollutants, and these can be extended to multipollutant studies. A tiered approach can be taken to refining exposure metrics used in multipollutant air pollution health effects studies, such as that outlined in Text Box 5.2. However, several different types of information are needed to support the application of these approaches, as described in following paragraphs.

Text Box 5.2 Example Tiered Strategy for Refining Estimates of Exposure

(From Neas and Özkaynak 2006)

Tier 1
- Simple Spatial Surrogates (source locations, e.g. GIS data, proximity to sources, or number or strength of sources within a buffer zone), and/or
- Ambient Monitoring data (e.g., central-site data on multiple pollutants)

Tier 2
- Air Quality Dispersion Models (e.g., hybrid modeling using multipollutant regional and local-scale models, such as CMAQ and AERMOD models)
- Land-Use Regression Models (cf., Jerrett et al. 2005a, b) for multipollutants that can combine available ambient concentration data with information on roadway, point source and landscape characteristics for estimating geographically or spatially resolved outdoor pollutant concentrations

Tier 3
- Intake Fraction Models (cf. Marshall et al. 2006) extended to multipollutants that can estimate the quantity of different pollutants inhaled by indi-

viduals over the course of a day as they move from one microenvironment into another. These models indicate the probability that an emission from a given source will be inhaled by an individual.

- Hierarchical Bayesian Models (cf. Fuentes and Raftery 2005) that can be used to combine multipollutant modeling results with measurements by using tiered Bayesian statistical estimation procedures

Tier 4

- Empirical Models (e.g., exposure predictions produced by using information on correlations between personal and ambient monitoring data, or exposure estimates based on time-activity weighted indoor and outdoor concentrations and using empirical estimates of indoor-outdoor concentration relationships)

Tier 5

- Mechanistic multipollutant exposure models (such as the SHEDS-Air Toxics model by EPA), that incorporate cohort and household specific information on micro environmental factors (e.g., indoor sources, housing information, air exchange rate, removal/penetration and infiltration rates, etc.) and exposure factors (e.g., time-activity data, inhalation rates, etc.)

Flexible Monitoring Programs. Mobile or more flexible local monitoring programs are needed, with an overall increase in emphasis on where (characterizing spatial distributions of concentrations—especially in relation to sources of interest) vs. what (more pollutants, chemical composition of PM) in terms of monitoring. Currently, spatial coverage of pollutant monitoring in North America is limited, and the vast majority of monitors are urban background monitors. This limitation may be addressed by conducting targeted monitoring campaigns in selected urban areas and across different seasons and years using a combination of mobile and fixed monitoring platforms in order to improve our understanding of spatial and temporal variation of pollutants in complex urban airsheds.

Time-Activity and Housing Surveys and Studies. Targeted time-activity surveys and exposure studies are needed to develop the factors and relationships to model the contributions of outdoor, indoor, and other sources to personal exposures to multiple pollutants. Such studies would include, for example, time-activity and population mobility/commuting surveys, micro-environmental measurements in key locations, housing surveys to understand infiltration factors, and questionnaires on type and use of HVAC systems, window opening habits. A few of the more focused or detailed surveys and monitoring programs may be repeated in some locations times or for certain population groups (e.g., vulnerable or demographic groups of concern), in order to examine the trends over time regarding changes in behaviors in activity, commuting and housing-related exposure factors. These studies will also support evaluation of the current atmospheric and personal exposure models and help refine and extend them to multiple pollutants of interest.

Personal Monitoring and Modeling. Adequate data on personal exposures to multiple pollutants are lacking. However, it is also necessary to develop both accurate and practical methodologies to be able to measure time-resolved (e.g., minutes to hour time scale) personal exposure concentrations of many of the particulate and gaseous pollutant species. Representative locations, populations and time periods will need to be monitored for a selected set of pollutants of concern. These data will then support development and refinement of existing and new multipollutant exposure models, such as the SHEDS model.

Understanding of Spatial and Temporal Variations. New information and techniques have to be developed to better combine available ambient monitoring data with measured exposure-related data and exposure model outputs to improve the characterization of the variation of PM and gases across seasons and geographic regions. These methods need to be generalized to broad geographic regions and a variety of multipollutant epidemiologic study designs, including multi-site observational studies or meta-analyses of panel studies conducted in different location. Specifically, different approaches or methods are needed to accommodate the biological time scales of interest and relevant epidemiologic study designs (e.g., prospective or retrospective longitudinal designs, time series, or cross-sectional designs) for multiple pollutants.

Expanding the Range of Pollutants Measured. There is some consensus that all components of PM are not equally toxic (NRC 2004). It is also likely that some unregulated gaseous species (e.g., some organic species) also adversely impact health. Indeed, a limited number of studies have found associations between VOCs and SVOCs and health outcomes (Mauderly and Chow 2008). There is no way, of course, that the health effects of these components can be studied by epidemiological methods unless they are measured in the environment (Text Box 5.2). Ambient measurements are also needed to determine the levels of exposure to these compounds as well. The major difficulty is in establishing priorities for the additional species which should be measured; the range of possibilities is enormous. This challenge points to the desirability of establishing pollutant groupings by general physicochemical class or type of biological reactivity. Such groupings may lead to identification of a practical number of index species representing exposure to the group.

Integration of Atmospheric and Exposure Models. Multipollutant atmospheric and exposure models need to be integrated with other data (e.g., air quality measurements, census, housing, transportation, etc.) in order to improve the temporal and spatial estimates of exposures to PM in the analyses of the relationships between ambient air pollution and adverse health outcomes. Techniques have to be developed to integrate data from ambient or source measurements into exposure models to best estimate air quality concentrations and personal exposures relevant to different types of air pollution epidemiology studies. In addition, spatial and temporal resolution of ambient air concentration data used in epidemiologic studies needs to be improved, for example by hybrid air quality modeling, hierarchical Bayesian modeling or fusion of measurement and modeling data, land-use regression modeling.

Biomarkers to Support Health Studies and Exposure-Dose Reconstruction. Biomarkers of certain non-criteria pollutants or their metabolites in the body are increasingly being developed and used in conjunction with community health studies. For criteria air pollutants however, there are few examples of these other than carboxyhemoglobin in blood from carbon monoxide exposures and cotinine in saliva or urine from exposure to environmental tobacco smoke. Recent CDC programs have begun producing a rich data base on biomarkers for the United States population (Barr et al. 2006), and gains might be made through interpreting these in the context of multipollutant exposures and risks. Exposure and dose reconstruction methodologies that are being developed for individual chemicals may be extended for multiple pollutants. Currently however, we have very few biomarkers of exposure that have been validated and are available for broad use. For greatest utility, markers not only need to be specific for a pollutant or pollutant class, they also need to be interpretable for reconstructing exposure-dose-response relationships. Only one example of the challenge is the difficulty in distinguishing between the influences of exposure (or dose) level and time since exposure, when exposures are intermittent or highly variable. Although it will be very challenging to validate markers for reconstruction of exposure-dose-response relationships, this is clearly an area for development.

5.4.2.2 Improving Assessment of Health Impacts

Several strategies can be considered for improving the assessment of health impacts. These include better understanding of the biological mechanisms underlying the observed outcomes. Indeed, one important aspect is the coordination of research efforts among the epidemiological, toxicological and exposure sciences. Probably the most important underlying need is leadership in developing a coordinated research program. The present research paradigm involves several independent efforts by several different research funding organizations in the NARSTO member countries. There has been no attempt to define jointly the greatest research needs to improve our understanding of the health-air pollution relationship and then to coordinate this research among the various research funding organizations.

Improving Knowledge of Causality. It is clear that contemporary levels of air pollution are associated with several adverse health outcomes in North America. The understanding of those specific agents that may be responsible for specific health effects is however, lacking. Clearly a multidisciplinary effort is needed to resolve this problem. Better characterization and measurement of ambient environments is needed, and toxicologists and epidemiologists need to work together to improve our knowledge in this area. Without more guidance from key groups and without coordination among investigators and research program managers, resolution of this issue is likely to linger. The leadership for this co-ordination must come from those funding the research; they define the areas in which research is most needed. Individual investigators will still have the freedom to carry this research out in the ways they consider to be most efficacious and scientifically sound. Funding agencies must also ensure that the creativity of investigators in not stifled as a result of co-ordination efforts.

Multipollutant Grouping Strategies. It is unrealistic to expect that we will soon understand causality (exposure-outcome relationships) for each of the hundreds of pollutants that almost certainly contribute to the health burden of air pollution. It has been sufficiently difficult to distinguish the causality of individual pollutants among even the few pollutants measured routinely to date. A shift toward a more integrated evaluation of the effects of a broader range of pollutant species intensifies this problem. One potential approach that must receive greater attention is the development of strategies for grouping pollutants for examining exposure-effect relationships and attributing causality. A more detailed knowledge of the spatial-temporal distribution of a greater range of pollutant species will present a better opportunity to characterize exposures by groupings such as physical-chemical class and source.

A contemporary example of grouping by physical class is the evaluation of the effects of PM mass, a physically and chemically complex class distinguished largely by its ability to be collected on filters. This has been a useful approach, despite the numerous sampling artifacts due to absorption and desorption of gases and vapors. It might also, for example, be useful to examine VOCs as a diverse class that might be integrated by collection and analysis methods. Classes that bridge multiple physical states might also be useful. For example, PAHs involve both particulate and non-particulate species. Indeed and especially near sources, semi-volatile compounds such as fluoranthene and several phenanthrenes exist simultaneously in the particulate and vapor phases.

Grouping by fundamental biological reactivity is another strategy needing evaluation, and which has received scant attention. It is expected that causal pollutants act through a limited range of initial physical-chemical interactions with target cells and fluids to trigger or promote complex series of biological response pathways resulting in the observed adverse health outcomes. It is uncertain, but certainly possible, that causal relationships might be better understood on this basis and that such relationships might be useful for guiding multipollutant management strategies. Such fundamental interactions may include, for example, oxidative injury, affinity for neural receptors, recognition by immune cells, or covalent binding to biomolecules such as DNA or proteins. It is not unreasonable to speculate that measurement devices might be developed that monitor the potential for a range of types of biological reactivity. Ongoing work to measure the oxidative potential of air (Venkatachari and Hopke 2007) signals a current move in that direction, based on evidence that oxidative injury initiates many biological responses. It is possible that new pollutant groupings based on biological reactivity, in addition to physical-chemical characteristics or source, might result from pursuit of this strategy.

Increasing Availability of Individual Outcome Data. Epidemiological studies that collect data from known individuals generally have better estimates of exposure, including the pollutants and concentrations, the length of exposure, and the relationship between exposure and periods of susceptibility such as childhood, pregnancy etc. Greater precision of health outcome and exposure data act to increase the statistical power to detect associations between air pollution and health. Future studies which collect individual-level data should be encouraged. Some funding must be devoted to health studies that collect data on individual exposures despite the fact that these studies are expensive to undertake.

Improving Systematic Collection and Availability of Outcome Data. Health outcome data are often collected for other purposes and are often not available or amenable to ready analysis. Relationships need to be fostered between the air pollution research community and organizations that collect health outcome data in an effort to make these data more available and amenable to analysis. Governmental agencies must resolve the conflict between the need to protect privacy of collected health data with the need to utilize these data for health research purposes. Clearly this issue can be resolved; collected health data have been successfully used for research purposes in the past without any evident breach of privacy issues. The impetus for resolution of this issue must come from then highest levels of the involved governmental agencies.

Improving Understanding of Exposure-Response Functions. The same methods that are used to help us understand what causes what can lead to a greater understanding of the exposure-response relationships. But the estimation of these functions also requires accurate measurement and exposure data and a greater understanding of the methods used to estimate these functions. Efforts to collect individual exposure data and an expanded set of pollutant data can also lead to greater precision in the dose-response estimates derived from statistical analyses. More attention has to be paid, however, to the influence of specific statistical approaches on the obtained estimates. Slight changes in methods or models can lead to major differences in the derived estimates. A more systematic approach towards understanding these differences is needed.

Improving Understanding of Biological Mechanisms. Although this domain has largely fallen to toxicologists, it is imperative that the toxicology be informed from the results of epidemiological studies, and that the latter make use of toxicological findings in their designs and in the hypotheses they consider. This is an area where funding organizations can also take leadership. Where epidemiological results need buttressing from toxicological studies, funding and guidance from funding agencies should support this effort. Similarly, funding is needed to ensure that the appropriate human studies are undertaken to increase our understanding and ability to interpret the results from toxicological studies.

The ongoing evolution of toxicological research tools (NRC 2007) will undoubtedly facilitate studies of the mechanisms of the effects of mixtures of air pollutants, improve the ability to predict synergisms, and aid cross-extrapolations between humans and non-human test systems. Advances in functional genomics, computational systems biology, physiologically-based pharmacokinetic modeling and knowledge of structure-function relationships should offer fresh approaches to examining the toxicology of mixtures and predicting the effects of mixtures beyond those studied in the laboratory (Andersen and Krewski 2009).

Improving knowledge of biological cause-effect time scales. The length of exposure needed to elicit health outcomes need also be investigated. This issue has largely been ignored, but is important if the public health is to be protected. In the epidemiological realm air quality data are often collected for other averaging times besides annual and daily timeframes. There is a need to consider some of the alternative timeframes in analyses. In particular, it would be desirable to consider relatively short (1 h or less) exposures and maximum hourly exposures in statistical analyses. These efforts should be accompanied by laboratory studies which examine the responses to short exposures.

Improving Understanding of Susceptibility. Studies have examined a myriad of health endpoints, ranging from respiratory and cardiovascular to developmental, reproductive, and even neurological endpoints in response to pollution exposure. Responses have been seen in all of these areas although the evidence for some responses is clearly more convincing than for others. What is not known is the extent to which existing health conditions make individuals more susceptible to air pollution exposure. The epidemiological literature clearly implicates the aged population as being more susceptible, and there is some evidence that the very young are an important susceptible group. Other studies have shown asthmatics and diabetics to be more susceptible. There is a growing interest in the use of genetic markers to help define susceptibility.

The EPA Interim Policy (EPA 2004c) states that "Genomics analysis is the study of all the genes of a cell or tissue, at the DNA (genotype), mRNA (transcriptome), or protein (proteome) level." This approach is contrasted with traditional methods involving the entire organism or only individual biochemical pathways. Genomics enable investigators to understand underlying biochemical mechanisms, provides sensitive measures of exposure and effects, and helps to identify genetic predispositions to effects. As an example, Kramer et al. (2006) examined the application of these principles in the context of asthma, identifying genetic biomarkers thought to play a role in allergic sensitization, disease development and disease severity. Similarly, data from Mexico City have pointed toward genetic susceptibility to ozone exposure in asthmatic children (Romieu et al. 2004b, 2006b). These were seen as potentially having implications for how sensitive subpopulations are defined as well as what constitutes an adverse health effect. Peden (2005) provides a review of genetic aspects of the response of asthmatics to air pollution. As yet, specific implications for multipollutant risk assessment and management have not been identified. Clearly both the genetic marker approach and some of the more traditional approaches need to be undertaken to better define our knowledge of the most susceptible individuals in our societies.

Improving Biomarkers of Effects. Despite the fact that no health outcome is known to be solely related to air pollution exposure, it would be helpful to define markers which are likely sentinels of disorders or disease that can be examined in future studies. Research to define such markers is clearly warranted. Some databases, such as the NHANES (National Health and Nutrition Evaluation Survey) in the United States could be exploited further in an effort to define biomarkers. This is of particular interest as this survey considers new measures and collects data periodically. Some discussion among the air pollution-health research community to define additions to this and similar surveys would be useful.

Ideally, a limited panel of readily-measured markers of effects could be identified that could be used to track the health impacts of pollution reduction strategies. Some measures have been used to link health outcomes to pollution in panel studies, such as the evaluation of relationships between carotid artery thickness and air pollution (Künzli et al. 2005) but may not be practical for widespread, repeated monitoring. There are two fundamental difficulties in achieving this ideal. First, the potential health effects of air pollution span such a range of diverse health outcomes that only a few types of outcomes could be monitored by specific markers. In the above example, carotid artery thickness may be a useful index of underlying atherosclerosis, by would not reflect several other types of adverse cardiovascular outcomes. Second, because air pollution is most likely a minority cause of many, if not most, outcomes with which it is associated, the poor "signal to noise ratio" would make it extremely difficult to disentangle the effects of pollution reduction from influences of other causes, underlying susceptibilities, and modifying factors that will also likely change with time. Continued exploration of useful markers of effect is warranted, but it will be challenging to develop markers that can be applied on a population basis.

Improving Comparability of Results from Different Studies. As discussed above, a greater commonality of study designs, analyses, and terminology would enhance intercomparisons among studies and integrated analyses (meta-analyses) of multi-study data. Leadership is clearly needed from research program managers and scientists to help resolve this issue. At present, there does not appear to be any comprehensive effort to address this issue. Again co-ordination of efforts among funding agencies could be used to promote commonality of designs. Absence this scientific organizations (e.g., International Society for Environmental Epidemiology or Society of Toxicology) could be approached to help set guidelines that would promote more comparability.

Improving Statistical Models for Attributing Effects to Pollutants Within Mixtures. Attributing health effects to individual pollutants within pollution mixtures is a very difficult statistical challenge, particularly when levels of the pollutants are highly correlated (Mauderly and Samet 2009). Fitting multipollutant models using conventional regression approaches often produces results that are difficult to interpret. Combined with the current regulatory focus on single pollutants, this difficulty has resulted in the development of separate risk estimates for individual pollutants, even when the different pollutants are measured in the same study. Significantly advancing our understanding of the combined risks of multiple pollutants present in mixtures, including their non-additive effects, will not only involve the data collection challenges noted above, but will also require advances in the statistical models used to interpret the data. The fundamental challenge is to determine whether the effects of the mixture differ qualitatively or quantitatively from the sum of effects estimated for the individual pollutants. The Health Effects Institute's recent solicitation for development of multipollutant modeling strategies (www.healtheffects.org) signals the beginning of what needs to be a growing initiative in this field.

5.4.3 Gains from Improved Interactions Between the Atmospheric and Health Research Communities

Progress toward a better understanding of the health impacts of multipollutant exposures will require greater communication and collaboration between the atmospheric and health sciences than has been typical. Although some scientists in both fields interact frequently with the other discipline, most scientists working in these fields do so less frequently than is needed to ensure adequate cross-education. An improved mutual understanding of current knowledge and capabilities would provide an improved conceptual foundation for prioritizing research and designing approaches in both fields. A better understanding of the full range of pollutant species, their distributions, and their concentrations would help health researchers to conceive hypotheses regarding cause-effect relationships and sharpen experimental designs. A better understanding of hypothesized and demonstrated pollutant-health links, including chemical features conferring biological reactivity, would help atmospheric scientists target key pollutants and design biologically-relevant measures of pollutant activity. An example outcome of cross-communication is the current effort to develop instruments to measure the oxidant potential of pollution (Venkatachari and Hopke 2007), in response to the current view among health scientists that oxidative injury is a triggering event for many biological responses. Finally, both epidemiologists and laboratory health scientists need to understand that different measurement methods used by atmospheric scientists may result in variables having identical common names, but in reality reflecting different pollutant species. The different methods used to characterize organic and elemental carbon are a contemporary example (Chow et al. 2001). Epidemiologists need to understand when air quality data are, and are not, comparable among different sampling efforts, and laboratory scientists need to understand how to link the composition of laboratory-generated atmospheres to ambient measurement data.

Interdisciplinary communication occurs at multiple levels, including reading papers published in other fields, personal interactions of senior scientists during advisory activities, interactions among investigators within research centers, and participation in discipline-based scientific meetings focused on other fields, and at topical interdisciplinary workshops. There is opportunity to enhance these interactions by convening additional workshops or sessions at meetings especially designed to update health and atmospheric researchers on advances in both fields.

Multidisciplinary research programs are common, but truly interdisciplinary research in which scientists from different disciplines work on the same studies rather than in parallel, is much less common. Strategies for integrating epidemiological and laboratory research were described in a preceding section. There are also several strategies for integration of atmospheric and health research tools, many of which are aimed at improved estimates of exposure to individual pollutants and combinations. These include:

- Increased range of sampling and analytical instrumentation having portability, cost, and analytical ranges practical for field studies
- More realistic design and more detailed characterization of laboratory exposure atmospheres containing combinations, complex mixtures, and reaction products
- Development of instrumentation to index exposure by biological reactivity (e.g., total oxidative potential, affinity for neural receptors, potential to disrupt metal homeostasis, covalent binding to biomolecules)
- Greater coordination to collocate measurement intensives with health studies
- Improved source apportionment models and expanded use to provide source-related exposure terms for health studies. (With caveats expressed in Sect. 5.2.1.3, alternative ways of grouping pollutants should also be explored.)
- Collaborative efforts to link characterization of microenvironments with time-activity profiles
- Increased contribution from biostatisticians in the design and sampling regimens for sampling networks, aimed at enhancing the design of health studies

5.4.4 Gains from Increased Collaboration Among Canada, Mexico, and the United States

Potentially important differences in exposure mixes and population susceptibility can be found among Canada, Mexico and the United States, particularly in contrasting Mexico versus Canada and the United States. These contrasts may provide opportunities for evaluating health effects relative to differences in multipollutant mixtures.

Levels of air pollution tend to be higher in some areas of Mexico than in Canada or the United States, and this is particularly true for ozone. Combined with the large populations in some of those areas (e.g., Mexico City), this may present an opportunity to examine exposure-response relationships over a greater range of exposure levels than is possible in either Canada or the United States alone.

Certain areas of Mexico have mixtures of pollutants that differ from those in Canada and the United States. An example is the high exposure of certain populations, and especially women and children in rural areas, to high concentrations of wood smoke during cooking. There may be differences in the predominant composition of PM between Mexico and the other countries, because of differences in emissions standards for fixed sources and the greater presence of certain industrial processes and sources in Mexico. There are also differences among countries in regulations regarding the use of toxic pesticides and herbicides. There is a yet-unidentified component beyond smoking that seems to contribute to lung cancer in Mexico (Ruiz-Godoy et al. 2007).

Epidemiologists collaborate among the three countries largely by participating jointly in studies conducted within a single country. Several studies in Mexico have resulted from such collaborations, and U.S. funding has also helped support studies in Mexico. These collaborations benefit all, but it would seem that all three countries might also benefit from a greater focus on integrative studies that includes populations (locations) in multiple countries in order to broaden exposure and demographic contrasts.

NARSTO has been successful in promoting communication among the three member countries in the atmospheric science community. There is clearly a need to extend this effort to communication and coordination of research programs and knowledge across the three countries. Whether NARSTO or some other organization is the appropriate mechanism to undertake this effort is unclear, but the need for this effort is urgent.

5.5 Establishing Realistic Expectations

It is important to establish realistic expectations for the ability of the health research community to advise development of multipollutant air quality management strategies and evaluate their benefits. Decades of epidemiological and laboratory research have revealed many associations between air pollution and health and confirmed the toxicity of a large range of air contaminants and pollution mixtures. Our current knowledge strongly supports the control of exposures to many pollutants, and the benefits of abrupt improvements in air quality or contrasts in exposure have been demonstrated in several “natural” and laboratory experiments. Present knowledge suggests the desirability of moving toward greater emphasis on multipollutant air quality management. However, it should be clear from the preceding information that many gaps remain in our understanding of the full range of health impacts of air pollution, the contributions of different pollutants to various health outcomes, the relative importance of different pollutants to shared outcomes, the importance of exposure to combinations of pollutants whose effects are super-additive, and exposure-dose-response relationships for both single pollutants and combinations. Much work remains to be done before we can confidently advise strategies to maximize total reductions in various health risks by limiting exposures to multiple pollutants.

A realistic assessment of current knowledge, key knowledge gaps, and key opportunities for progress is essential to the development of research strategies and prioritization of research resources. It is also important for identifying areas that could benefit from greater interactions between the health and atmospheric science research communities. It is important to acquaint the decision-makers with the bounds of current knowledge, the likelihood of assistance from the health community in designing and defending multipollutant air quality management and accountability strategies, and the likely time frame for substantive improvement in knowledge.

5.5.1 Current Status and Future Programs

Two fundamental questions dominate the many current health information gaps and research needs limiting our progress toward further implementation of multipollutant air quality management: (1) "what causes what?" and (2) "are combinations of pollutants important?" Most current effort can be viewed as largely focusing on the first question, with much work remaining to be done. Some, but little, effort has been devoted to the second question. Although different multipollutant air quality management strategies raise different specific questions that need to be addressed by different experimental designs, these two questions are fundamental to most, if indeed not all, multipollutant health research.

We do not have a very good ability to parse the contributions of myriad pollutant species to the many adverse health outcomes associated with air pollution. We know from epidemiology that some criteria pollutants are more strongly associated than others with different health outcomes, and laboratory studies have demonstrated a range of effects of a much broader spectrum of air contaminants, including air toxics. However, the lack of exposure data for most air contaminants, the imprecision of population exposure estimates, the focus of most studies on a small portion of potential health outcomes, and the scarcity of head-to-head comparisons of the effects of different pollutants leave us with limited ability to confidently assign qualitative, as well as quantitative, health impacts to the breadth of pollutants that are undoubtedly affecting health.

Present knowledge tells us that individual pollutants can have multiple effects and multiple pollutants can have the same effects. The range of health effects associated statistically with pollutants will likely continue to expand. The majority of pollutant species are not measured routinely and we have limited or no health information for many of them (e.g., air toxics, VOCs, SVOCs, secondary organic aerosols, unresolved complex organic mixtures, short-lived reactive species). Such knowledge is fundamental to more precisely targeting air quality management strategies toward reducing specific health outcomes, and is especially critical to prioritizing pollutant classes and species (and thus sources) for multipollutant air quality management strategies aimed at reducing health burdens. Such knowledge is also important in accounting for the health benefits of pollution controls. For example, demonstrable benefits may not reach expectations if non-targeted and unmeasured pollutants are responsible for a portion of the effect attributed to the targeted species.

We have some, but very limited, knowledge of whether combinations of pollutants exist that are important because their effects are non-additive. Combinations whose effects are greater than additive (i.e., synergistic) would be of particular interest. We know from laboratory studies that such interactions are plausible and some likely occur, although laboratory studies of combined exposures have most typically suggested additive or less than additive effects. If non-additive combinations exist, an evolution of risk-based multipollutant air quality management and accountability strategies must inevitably take them into account. The modest effort to evaluate the effects of combined exposures to multiple pollutants has been directed primarily toward criteria pollutants, and needs to expand to include other species.

The extent to which we may be missing opportunities for health gains by misattributing causality or failing to identify the full range of pollution effects is not known. It is not likely that we fully understand the benefits of reducing exposure to even the single pollutants that have received the most research and regulatory attention, much less the broader spectrum to which people are actually exposed. Although we have learned much and our efforts may have indeed focused on the most important pollution-health associations, our current knowledge does not assure this.

5.5.2 Progress to Be Expected in the Next Ten Years

The nature and extent of progress during the next decade in our understanding of air pollution-health relationships and the benefits of reducing exposures will depend heavily on the strategies, incentives, and resources provided by research sponsors. It is important to understand that 10 years is not a very long evolutionary period in the research world, and that research is an iterative process. For example, it typically requires more than a year for research sponsors to assess current information, set priorities, and issue solicitations for investigator proposals, another year to initiate funding for selected grants or contracts, and multiple years to complete work under each agreement and publish results. Ten years is sufficient for only two, or at most three, cycles of planning, funding, and completion. Although the breadth of issues addressed, the number of research groups involved, the scope of research tools applied can be increased somewhat in proportion to funding, the length of research cycles cannot be shortened markedly. However, assuming an appropriate shift of emphasis combined with resources similar in magnitude to those provided over the last decade, we can anticipate meaningful advances over the next decade.

5.5.2.1 Exposure Specification

Advances in our ability to estimate individual and population exposures will occur largely through studies involving special (non-regulatory) measurements of microenvironments using stationary outdoor and indoor monitors and personal monitors. Measurements of an expanded range of physical-chemical species will address noncriteria, as well as criteria pollutants (including increased attention to bioaerosols). We will gain a better understanding of not only the spatial-temporal variability in concentrations of pollutants, but also the degree of similarity of such variability among different cities and rural regions. We can expect that exposure models will increase in sophistication by incorporating more detailed characterization of exposure microenvironments and time-activity data. The generation of improved time-activity data will provide a progressively increasing ability to model exposures of both general populations, activity-based subpopulations (e.g., homes, commuting routes, workplaces, and schools), and subpopulations having special susceptibility (e.g., children, elderly, disease-based groups, and pregnant women). There should be more extensive validation of exposure models by comparison to measured values. The incorporation of a greater spectrum of pollutants will enable development of multipollutant exposure models.

5.5.2.2 Understanding What Causes What

Two developments should lead to improvements in more accurately attributing health effects to a wider range of pollutants, although it is unrealistic to expect that the full spectrum of pollutant species will be addressed within a decade. First, the above improvements in exposure specification combined with shifts in research emphasis will facilitate the ability of epidemiologists to evaluate exposure-response relationships for general populations and subpopulations in greater detail and with more pollutant specificity. In parallel, there should be advances in the availability and quality of data for an expanding range of health outcomes. The result will be increasing clarity concerning of the relative contributions of different pollutants and pollutant classes to a broader range of health outcomes. Second, shifts in the emphasis of laboratory research toward more systematic exploration of cause-effect and dose-response relationships will improve our understanding of the pollutant species and classes driving the mechanisms leading to different health outcomes. Laboratory research will continue to encompass a range of observational and hypothesis-driven strategies, but gains will be achieved by increased emphasis on direct comparisons of effects and underlying mechanisms among different pollutants. There will be increased emphasis on more recently-discovered pollution-health relationships (e.g., extrapulmonary vascular effects, effects of in utero exposures, specific genetic predispositions). Advances in the emerging field of computational toxicology will offer expanded experimental approaches and improved pathways for extrapolating findings between toxicological models and humans. Closer communication and collaboration between epidemiologists and laboratory researchers will facilitate the “hand-off” of results, hypotheses, and research strategies, and result in a more coherent combined effort than has been typical of the past.

5.5.2.3 Understanding the Importance of Combinations of Pollutants

Advances will be achieved both as a by-product of the above research and as a product of explicit focus on combinations of pollutants. A limited analysis of combined effects will be inherent to refined analyses of the contributions of an increasing range of individual pollutants to an increasing range of effects. Although a predominant emphasis will continue to be on linkages between individual pollutants and pollutant classes and health outcomes, an increasing minority portion of resources will be directed explicitly toward exploring the importance of combined exposures. The majority of this emphasis can be expected to occur in the laboratory, taking advantage of controlled exposures to both complex mixtures and simple combinations. It can be expected that increased evidence for synergistic effects among representatives of major pollutant classes will be produced, if indeed, such interactions exist. Advances in understanding multipollutant effects will be modest in comparison to greater progress in attributing effects among single pollutants. However, whether or not some clearly synergistic interactions are identified will strongly influence research and regulatory agendas during the following decade.

5.5.2.4 Grouping Pollutants by Biological Reactivity

With increased awareness of this issue, advances in our understanding of the fundamental mechanisms by which pollutants trigger health responses will likely improve our understanding of the extent to which pollutants may be usefully grouped for management on the basis of the nature of their fundamental biological reactivity. Because effort to measure oxidative potential of ambient air has recently been initiated, it is expected that exploration of this fundamental characteristic will be among the first types of biological reactivity to be evaluated. It can be expected that workshops and individual research groups will identify other promising approaches and that exploration of the utility of other markers of biological reactivity will be underway within the next decade.

5.5.2.5 Importance of Chronic Exposures

We can expect some advancement in our understanding of the importance of chronic exposures, and the relative contributions of short- and long-term exposures to different health outcomes. Owing particularly to challenges related to assessing long-term exposure and ascertaining changes in health status of study participants over many years, there have been relatively few epidemiological studies of effects of long-term exposure. Ensuring that air quality management effectively reduces the risks associated with long-term as well as short-term exposure will require considerable effort to expand the evidence base in this area. New prospective epidemiological studies of long-term effects will be initiated, but cannot be completed within 10 years. However, there will be a continuation of the present effort to evaluate data from ongoing studies and to identify existing sources of exposure and outcome data that can address long-term exposures. Although chronic studies of animals exposed to pollutants are feasible, they have been rare owing to their length and cost. A new long-term study of emissions from advanced technology diesel engines will be completed in 2011 (HEI 2007b). A very limited number of chronic animal studies addressing other pollutants or mixtures might be initiated during the decade.

5.5.2.6 Knowledge of Health Outcomes

At least limited improvement in the availability and quality of population health outcome data can be expected during the coming decade, largely as a result of a move toward comprehensive national health care systems in the United States and Mexico. The broader scope and more readily availability of data generated by Canada's national health care system demonstrates that movement toward nationalized health care can be expected to improve data availability. It is not clear to what extent or how rapidly such changes may occur, but movement in that direction is likely. Based on past experience, epidemiological studies taking advantage of both changes in "administrative" health data systems and greater scrutiny of existing data sources are likely to reveal relationships between pollution and an increased spectrum of adverse health outcomes.

5.5.2.7 Knowledge of Susceptibility

We can expect continued refinement of our understanding of factors that render individuals sensitive to the health effects of pollution. Just as the past decade clarified that subjects with pre-existing cardiovascular disease constitute a susceptible subpopulation, and pregnant women likely constitute a group of special concern, it can be expected that additional susceptible groups will be identified. Our understanding of fetal sensitivity to effects of mothers' exposure, and the effects of exposure on postnatal development and growth will be improved. Additional genotypes associated with increased susceptibility will undoubtedly be identified. We will also improve our understanding somewhat of the influences socio-economic status and nutrition. In aggregate, this growing knowledge base will inevitably result in iterative consideration of approaches to implementing regulatory mandates to protect sensitive populations.

5.5.2.8 Accountability

Increased effort to assess the effectiveness of air quality management strategies in reducing pollution-related health burdens can be expected. Grants, contracts, and internal federal programs aimed specifically at evaluating the benefits of past air quality improvements will result in advances in methods. The primary focus will shift from using results of "natural experiments" to support the benefits of pollution reductions to analyzing the effects of longer-term changes in air quality. It is likely that, in addition to individual investigator-initiated studies, national agencies will conduct assessments, develop substantive reports of findings to date, and implement systematic, serial assessment strategies.

5.5.3 *Caveats Concerning Unrealistic Expectations*

Although much progress can be expected, considerable work will remain to be done on all of the above issues beyond 10 years. Science is incremental and shifts of emphasis, development of new strategies, and iterative responses to new findings will take longer than 10 years to complete. It would be unrealistic, for example, to expect:

- Validated exposure models for more than a limited number of pollutants, microenvironments, and subpopulations;
- An understanding of the full range of health impacts of all air contaminants, including exposure-response relationships and thresholds;
- Confidence in quantitative estimates of the dose-response relationships between air pollution exposures and health responses without considerable uncertainty bounds;
- Confidence that all important synergies have been identified, or confirmation that none exist;
- A few readily-measured markers of effect by which the benefits of pollutant reduction can be confidently assessed;
- A highly accurate valuation of benefits of past air quality improvements;
- An ability of the health research community to prescribe multipollutant air quality management strategies that ensure that health returns of control strategies are yet fully optimized.

To a large extent, the rapidity of progress will depend on the will and ability of research sponsors to ensure that resources are directed to efforts that will result in the greatest advancement toward support of multipollutant air quality management goals. Given early and continued attention to allocation of resources, much progress could be made over the next 10 years in our understanding of the relationship between health and exposure to multiple air pollutants. There can be little question that movement in this direction is warranted. However, achievement of the ultimate goal of establishing risk-based multipollutant air quality management strategies that ensure the greatest health benefit per unit of air quality management resources and validating that optimization through measurements of health gains will be a several-decade process. That process will likely reach a practical limit with respect to competing priorities long before it might be considered to have been accomplished in full.

5.6 Conclusions

The overall conclusion of this chapter is that our present understanding of links between air quality and health provides only a limited basis for supporting the evolution toward multipollutant air quality management and assessing its effectiveness. This is both a reflection of the natural course of progress in the air quality, exposure, and health sciences, and a product of the historically dominant orientation of air quality management toward single-pollutants and sources. Air quality health research to date has provided a continuously-improving understanding of the relationships between air quality and health. Improvements in air quality over past decades achieved by management strategies predicated on evidence of health risks have undoubtedly reduced the health burden of air pollution, whether or not the benefits have been accurately measured. Current knowledge limitations are not unique to the integrated consideration of multiple pollutants; they also pertain to improving knowledge about the effects of single pollutants. The importance of further refining our understanding, however, increases in proportion to the increase of emphasis on attributing health risks among more pollutants and combinations of pollutants, and evaluating the health benefits of evolving management strategies.

The two fundamental issues (questions) regarding the health effects of air pollution can be stated succinctly as: (1) "what causes what?" and (2) "are combinations of pollutants important?" Uncertainties about which pollutants cause different effects and the relative impacts of air pollution and other factors need to be reduced to better inform and assess multipollutant air quality management. Attention to potential non-additive interactions among combinations of pollutants is integral to refining the attribution of causality among an increasing range of pollutant classes and species.

The full scope of the health effects of criteria pollutants is likely not yet known, and there is much greater uncertainty about the range and magnitudes of the effects of non-criteria pollutants. We have sparse exposure data for the majority of pollutant species and a limited understanding of the range of health effects that they might cause.

Better characterization of exposure is the single most pressing need for advancing air pollution epidemiology beyond its present state. We need better spatial-temporal characterization of general and localized environments and a better understanding of the time-activity patterns of different populations of concern. The substantial improvements in exposure models necessary for correctly attributing effects among a broader range of pollutants and combinations will require more detailed input data than presently exist.

Multipollutant air quality management could benefit greatly by improved strategies for grouping of air pollutants by class, source, biological reactivity, health outcome, etc. It is implausible that risks will be identified or tracked by each of the myriad individual physical-chemical pollutant species. Groupings of pollutants that are most useful for health effects may differ from the groupings most useful for ecological effects, source apportionment, or emission control. Moreover, different grouping strategies are likely to be optimal for different categories of health outcomes.

A better understanding of biological mechanisms could facilitate the identification of causal pollutants and the grouping of pollutants by initial biological reactivity, common response pathways, or similar health outcomes. Much-needed improvements in biomarkers of exposures and effects can also come through studies of mechanisms.

There have been some, but not many, attempts to implement accountability strategies that directly evaluate the health benefits of improvements in air quality, rather than projecting benefits from estimated exposure-response relationships. The most frequently cited evidence for health gains have resulted from instances of marked, rapid changes in air quality. The benefits of slower incremental changes are more difficult to evaluate, because other factors affecting the same outcomes change over the same time period. However, some useful strategies have been pursued, and more can be developed as our understanding of pollution-health relationships improves.

Improved and more extensive partnerships between the atmospheric science and health science communities would not only be useful, but are also essential to substantially improving our knowledge of the health impacts of air pollution and the guidance of multipollutant air quality management strategies. Opportunities for greater linkage of these research communities encompass conceptual, technical, and experimental issues.

The requirement for financial support is paralleled by a need for strong leadership to ensure that research resources are deployed in strategies that can most effectively inform multipollutant air quality management and accountability. The scope of potential research is so broad that care must be taken to avoid a "random walk" of studies producing information that is difficult to integrate. The providers of research support are ultimately responsible for establishing a matrix of information needs and directing resources in a manner that ensures that the most critical points of the matrix of information gaps are addressed. The research strategy should be forward-looking, and not constrained by present regulatory structure. Such high-level management need not be in conflict with research creativity and competition.

With sufficient attention to the strategic direction of research resources toward the issues described in this chapter, substantial progress can occur within a decade. However, progress toward a better understanding of the health impacts of a broader range of pollutants, and an improved ability to assess the health benefits of air quality management strategies, will be incremental and iterative over a period of several decades. Although the idealistic goal of fully apportioning health impacts among all air contaminants and their combinations will likely never be reached, the ability to inform and assess air quality management strategies can unquestionably improve well beyond its current state.

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Chapter 6
Ecosystems

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North America extends from the Arctic Ocean in northern Canada and Alaska south to Panama, though Mexico is considered the southernmost extent of North America in this assessment. This land mass also extends from the Island of Newfoundland in the east to the Aleutian Islands in the west. North America has been divided into 15 broad ecoregions that each contains broadly similar communities of terrestrial and aquatic plants and animals that have adapted to fit the climate and soil of the sites where they are found (Bailey 1998). The region encompasses a wide range of climate and ecosystems types including Arctic tundra in northern Canada and Alaska, boreal forest, the Canadian prairies and American plains, temperate forests in eastern and western Canada and the United States, arid and semi-arid regions of the southwestern United States and northern Mexico, as well as tropical wet forests in southern Florida and in Mexico.

North America is inhabited by more than 500 million people of whom more than 75% live in urban areas (UNEP 2007). These urban regions with additional contributions from rural regions generate a complex mix of gaseous, dissolved and particulate chemical species, which include sulfur and nitrogen, acidic and oxidizing compounds, trace metals such as mercury, lead, and cadmium, and a wide variety of deleterious, volatile organic substances which are produced by industry, transportation and power generation (UNEP 2007). The transport and deposition of these air pollutants varies widely across the continent depending on population density, the number of mobile and stationary sources as well as climatic patterns and topography. In addition to pollutants described above which are generated within the continent, North America also receives mercury and organic pollutants in air and precipitation that originate through long-range transport from other continents (UNEP 2007).

Direct effects of gaseous and suspended air pollutants on microorganisms, plants, animals and humans are not the only source of stress to ecosystems, as deleterious

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effects also occur from air pollutant interactions with soils. Wet and dry deposition, fog and cloud deposition all contribute to cause adverse impacts on terrestrial and aquatic systems, and are associated with unique processes and effects, many of which are not well understood.

Observable deleterious effects of air pollutants on ecosystem health and function date at least to the first Industrial Revolution in eighteenth century Europe (McNeill 2001), but effects were only observed later in North America, dating to the mid- to late nineteenth century when damage to vegetation downwind of the Sudbury region of Ontario and in other metal smelting regions were first observed (Baes and McLaughlin 1984; Winterhalder 1995). The scientific documentation of air pollutant effects on vegetation in North America is an even more recent phenomenon dating to the 1960s when extensive damage to the boreal forest near the Sudbury smelter was reported (Gorham and Gordon 1960). The study of air pollutant effects on aquatic systems in North America is an even more recent phenomenon as studies on the acidification of surface waters by acid deposition first began to appear in the 1970s (Beamish and Harvey 1972; Cronan and Schofield 1979), and the first international conference on the ecological effects of acid rain was held at Ohio State University in 1975 (Dochinger and Selliga 1976).

The complex patchwork of air pollutant sources, transport, deposition, and toxicological effects, superimposed on a landscape of varying ecosystems does not allow an easy generalization of air pollutant effects in North America. In this chapter, we approach this challenge by identifying the major air pollutants which have widespread and documented effects on terrestrial and aquatic ecosystems in North America (acidification, metal contamination, ground level ozone, persistent organic pollutants), and highlight the ecosystems and regions which are most affected. We then describe how air pollution effects were first recognized, the current extent of their effects (Sect. 6.1), and any significant changes or trends that have been identified over time (Sect. 6.2). We also describe past and current monitoring programs that document the ecosystem effects of air pollutant ecosystem effects as well as some of the predictive ecosystem models which allow us to determine how these effects might vary with changes in air pollutant stressor intensity. Consistent with the overall themes of this NARSTO assessment, we discuss known and likely multipollutant interactions that affect ecosystems. Finally, we make recommendations concerning future monitoring and research priorities and directions.

6.1 Major Air Pollutant Stressors Affecting North American Ecosystems

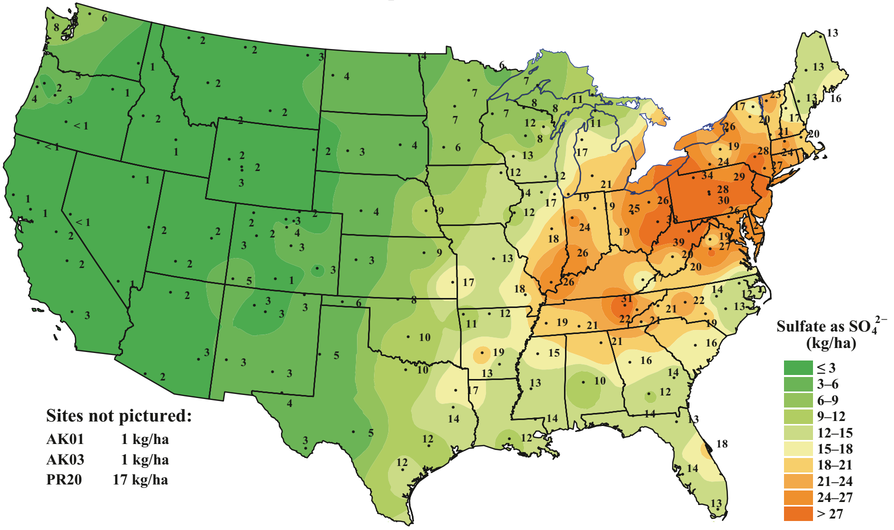
6.1.1 Acid Deposition

Acid deposition is a general term that describes the deposition of strong acids and oxides from the atmosphere in rain and snow as well as in gaseous and particulate form that primarily originates from human activities. Sulfuric and nitric acids are the dominant forms along with small amounts of hydrochloric acid. Sulfur originates mainly from the combustion of fossil fuels (primarily coal) for energy generation and the processing of metal ores, while the main source of nitrogen are transportation, power generation and agricultural use of fertilizers and intensive animal husbandry. The terms wet and dry deposition are used to distinguish rain and snow from gaseous and particulate forms; cloud or fog water deposition is often treated separately where this form is measured. Pure rainwater has a pH of about 5.66 due to the dissolution of carbon dioxide to form carbonic acid (Drever 1997; although the concentration of carbonic acid in precipitation has increased in recent decades due to greenhouse gas emissions). Determining the "natural" pH of precipitation is difficult because other sources such as dimethyl sulfide from oceanic algae, natural organic acids from wetlands, and alkaline windblown dust can affect pH values to a varying extent in different locations (Charlson and Rodhe 1982). Background pH values therefore can vary regionally in North America from 4.5 to >7 so that as a result, some researchers consider a pH value <5.0 to be a general indicator of acid rain (Charlson and Rodhe 1982). In northeastern North America, the pH of precipitation may have been >6 before humans began to greatly affect regional atmospheric chemistry (Cogbill 1976).

Ammonium (NH_4^+) is also an important component of atmospheric nitrogen deposition, and concentrations in wet deposition have been increasing since the 1980s across large parts of the U.S. Midwest and Southeast (Lehmann et al. 2005). These increases are of concern because NH_4^+ contributes to acidification and nutrient enrichment of ecosystems (Stoddard 1994) and is also linked to particulate matter formation. Ammonium deposition poses a challenge for the scientific and regulatory communities in North America. First, a significant amount of reduced nitrogen emissions in the form of NH_3, can be transported in the gaseous or particulate phase and later deposited to ecosystems as dry deposition. The principal dry deposition network in the United States, CASTNET, does not currently monitor NH_3 deposition, so deposition levels are not known with great certainty. Additionally, emissions of NH_3 and NH_4^+ are dominated by livestock (~55% of U.S. emissions) and fertilizer (~26% of U.S. emissions) sources (EPA 2005), in contrast to NO_x, SO_2, and mercury, which largely originate from either mobile and/or stationary power plant and industrial sources. These emission sources are not regulated in the United States or Canada despite an acknowledged role in ecosystem acidification and in nutrient enrichment, especially in downwind locations close to concentrated animal livestock facilities (Aneja et al. 2006).

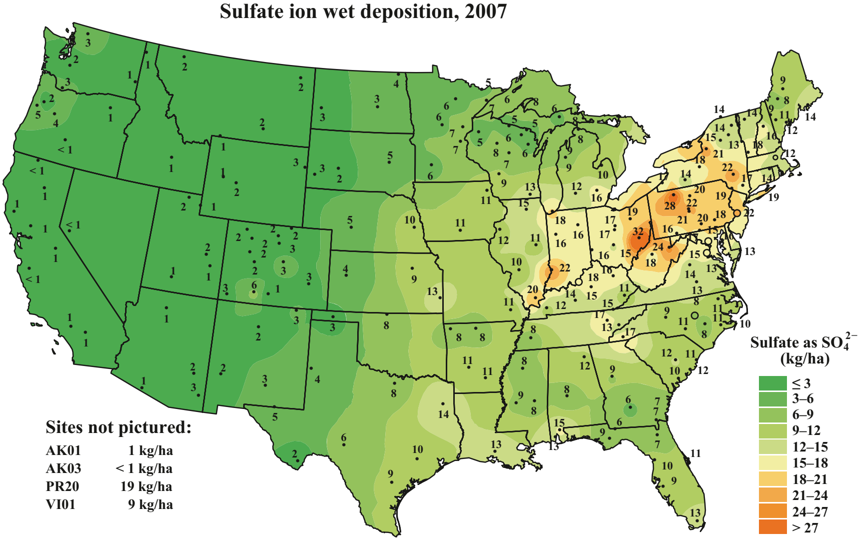
Spatial and temporal patterns of atmospheric deposition vary widely across North America (Fig. 6.1). When widespread data first became available for eastern North America in the 1970s, acid rain was about 65% sulfuric acid, 30% nitric acid, and 5% hydrochloric acid (Cogbill and Likens 1974). In contrast, deposition of nitrogen in the Rocky Mountain region of the United States generally exceeds that of sulfur on an annual mass basis (Fig. 6.1). Deposition of sulfur has declined by about half in most locations in North America from the 1980s to 2005–2007 (Nilles and Conley 2001; Lehmann et al. 2005; EPA 2007a; perhaps with the exception of Mex-

Sulfate ion wet deposition, 1994



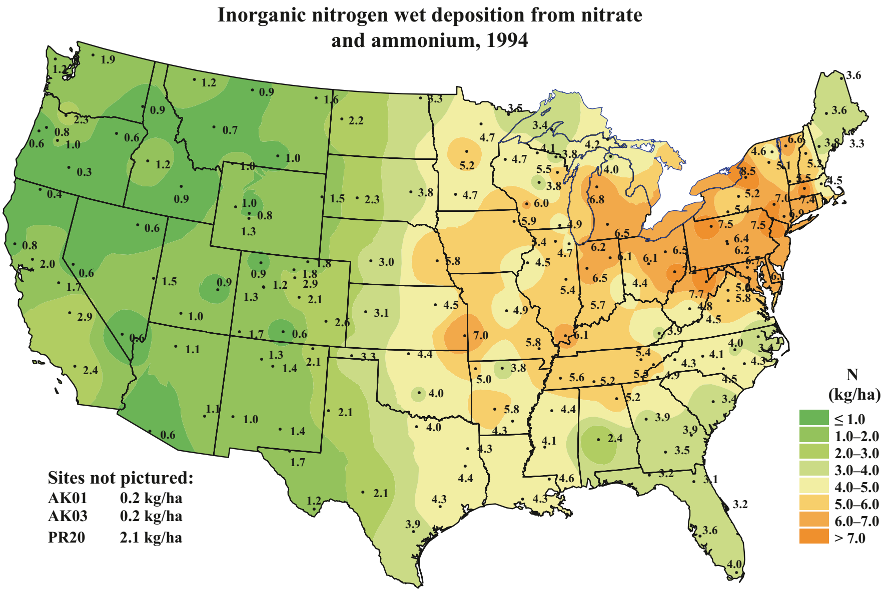
National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Sulfate ion wet deposition, 2007

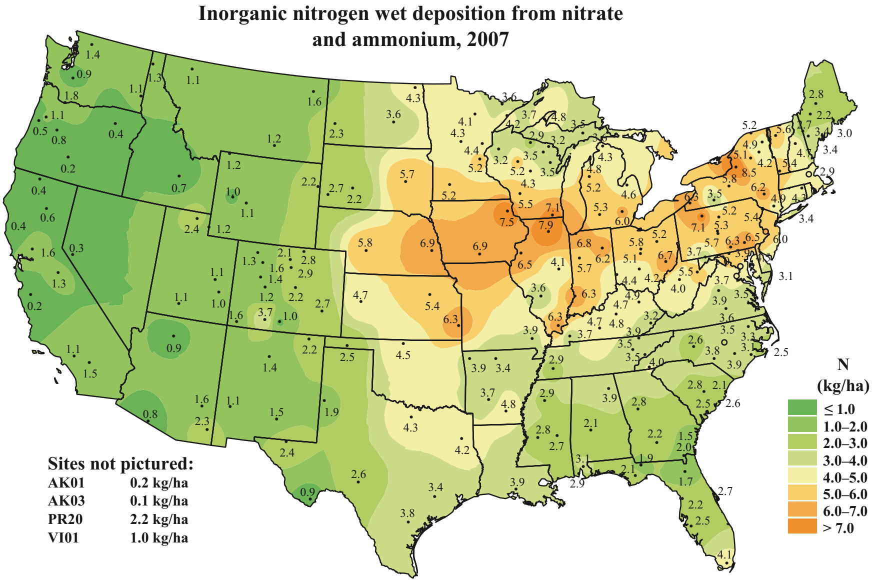


National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Fig. 6.1 Wet deposition of sulfate and inorganic nitrogen (nitrate and ammonium) in 1994 and 2007 as determined by data collected by the U.S. National Atmospheric Deposition Program. (NADP 2009)



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Fig. 6.1 (continued)

ico for which continuous data are sparse), whereas trends in nitrogen deposition vary more widely with location. For example, wet deposition of inorganic nitrogen has generally decreased by <30% across eastern North America, whereas increased deposition has been reported in parts of the Midwestern and Rocky Mountain regions of the United States (Lehmann et al. 2005; EPA 2007a). One result of these contrasting patterns in trends is that acid rain in recent years consists of an increased proportion of nitric acid relative to sulfuric acid than was evident in the 1970s and 1980s (Lehmann et al. 2005).

Acid rain effects were first recognized as a problem for soils and freshwaters in North America in the 1960s through measurements at the Hubbard Brook in New Hampshire (Fisher et al. 1968; Cogbill and Likens 1974). Subsequently, measurements collected from several locations in North America in the 1970s revealed that acid rain was widespread east of the Mississippi River in the United States and east of the Ontario-Manitoba border in Canada, with many locations reporting pH values between 4 and 4.5 (Cogbill and Likens 1974; Likens and Bormann 1974). Acid rain was also later documented in the Rocky Mountain region, and in urban areas along the Pacific coast (Glass et al. 1979; Lewis and Grant 1980). Acid rain had previously been identified in Scandinavia and linked to long-range transport of sulfur and nitrogen emissions from industrial sources in central and eastern Europe, as well as the United Kingdom (Oden 1968), and a similar long-distance transport pathway was identified in North America for emissions originating largely from coal-fired power plants in the Midwestern United States and metal smelters in Canada (Cogbill and Likens 1974; Beamish and Harvey 1972).

Further work in the 1980s as part of the National Acid Precipitation Assessment Program in the United States, and Acid Rain Assessments in Canada, conclusively demonstrated that acid rain in northeastern North America originated largely from stationary sources to the west that were dominantly coal-fired boilers (Venkatram and Pleim 1985). Ecological research during the 1980s also conclusively demonstrated that ecosystem acidification and degradation was caused by acid rain (Schindler 1988).

The primary cause of deleterious acidification effects to ecosystems occurs when soils are unable to neutralize hydrogen ions and associated aluminum ions through base cation exchange and chemical weathering reactions (Driscoll et al. 2001). Acid precipitation can be readily neutralized if a rapidly weatherable mineral such as calcium carbonate is abundant in soils and bedrock. Even less weatherable silicate minerals such as plagioclase feldspar can also be effective in raising the pH of acid precipitation to a value of >6 in surface waters, a level at which deleterious aquatic ecosystem effects are minimal. In soils that lack rapidly weatherable minerals, the principal source of neutralization is cation exchange of hydrogen ions and aluminum for the base cations calcium, magnesium, sodium, and potassium held on organic matter and clay surfaces.

This cation exchange process can be quite effective at neutralizing acidity, but loses its effectiveness as the base saturation (percent of cation exchange capacity occupied by base cations) declines due to continued acidic inputs (Likens et al. 1996). Replenishment of base cations lost through exchange and transport out of the ecosystem is dependent largely on the weathering of bedrock at a rate rapid enough to maintain soil base saturation and to a lesser extent through the atmospheric deposition of cations. In some geological settings with low rates of base cation replenishment to soils, recovery from acidification is slow, even with rapid decreases in acid deposition loads. In summary, ecosystem sensitivity to acidification depends not only on the amount of acid deposition, but fundamentally on the neutralizing capacity of soils and the weathering rate of the underlying bedrock and/or till to allow recovery of exchangeable base cations.

In addition to the rate of acid deposition, soil mineral weatherability, and soil exchangeable base cations mentioned above, several other factors affect ecosystem acidification. These include elements of geomorphology such as elevation and slope, climate, glacial history, vegetation, and the history of human landscape disturbance (Landers et al. 1988). Together, these factors define geographic areas in North America that are particularly sensitive to acidification (Omernik and Powers 1983). In general, vulnerable areas tend to be in forested regions underlain by resistant bedrock such as the Canadian Shield, the Maritime Provinces and northern New England, the Adirondacks of New York, the central Appalachian Mountain region of Pennsylvania, West Virginia, the Upper Midwest, and the Blue Ridge Mountains of Virginia, Tennessee, and North Carolina, as well as the Grand Tetons and the Sierra Nevada in the western United States (Shilts 1981; Driscoll and Newton 1985; Sullivan et al. 2008; McNulty et al. 2007).

Much of the landscape west of the Rocky Mountains is arid or semi-arid. The Pacific Northwest, known for its wet winters, also has very dry summers typical of Mediterranean climates. Annual precipitation amounts in western North America increase northward with arid conditions of less than 26 cm at the U.S.-Mexican border to as much as 260 cm at the Canadian-U.S. border. Given the arid climate in the Southwest, it is not surprising that dry deposition of air pollutants plays a more significant role in total deposition in the southwest United States and in Mexico than it does in the east. The initial work on air pollution effects to western U.S. forests was started in the 1960s in the San Bernardino Mountains surrounding the Los Angeles Basin. At the time, ozone (discussed later in the assessment) was the pollutant of concern, but since the 1980s, nitrogen deposition (primarily from fog, cloud and dry sources) has been an important focus of research studies. Although the effects of nitrogen deposition are universal, the relative amount of water that accompanies this deposition makes an important difference in terms of detecting and monitoring effects. Many streams in the west are ephemeral, flowing only during rains and snowmelt in winter and spring, but drying up by early summer. Thus, stream monitoring for nitrate as an indicator of nitrogen saturation is more challenging in these arid settings; nonetheless, studies in the west have shown large fluxes in ephemeral stream water nitrate concentrations that are correlated to high atmospheric loads (Fenn et al. 1998; Meixner and Fenn 2004).

The mean annual pH of precipitation in Mexico varies widely from 6.48 in the predominantly agricultural Guanajuato State to 4.6 in coastal Veracruz State (Baez et al. 1989) and the effects of acidification in heavily polluted parts of Mexico such as the Mexico City valley are different from those known to occur in the wetter, northern parts of the continent, as well as in less polluted portions of the U.S. Southwest. The first studies of acid deposition in the Mexico City valley were conducted in the early 1980s and showed significant acidity levels (Bravo 1987; Paramo et al. 1987).

Currently, acidic atmospheric deposition has been detected in several ecosystems affected by air pollutant dispersion from either populated urban or industrial areas. The vulnerability of important forest types in Mexico (pine forest, 2350–4000 m above sea level (masl), fir forest, 2700–3600 masl, oak forest, 2350–3100 masl, cloud forest, 2500–2800 masl, juniper forest, 2450–2800 masl, and scrub oak forest, 2350–3000 masl) to acidification is high, and these systems have the potential to become highly disturbed and stressed, as well as susceptible to insect damage. Moreover, the soil depth, clay content, pH, and cation exchange capacity decrease with increasing elevation, which potentially increases the impact of acid deposition in higher elevation forests (Marin 2002). Additionally, agricultural crops such as mango have been shown to be susceptible to fungal pathogens downwind from sources of acidic emissions and diesel ash (CFE Report 2003).

6.1.2 Ecosystem Acidification

Ecosystem cycling rates of atmospherically-deposited sulfur are affected in large part by a region's recent glacial history. Soils in the north and in high elevation locations in the west have been glaciated as recently as about 12,000 years ago, whereas soils in the south are much older and more highly weathered. This difference in glaciation history as well as the warmer climate in the south, generally results in a thinner organic soil horizon in the south, and a greater amount of iron and aluminum hydroxide in the mineral soil, with a large capacity to adsorb atmospherically-deposited sulfate (Rochelle et al. 1987). Additionally, the longer growing season and higher ecosystem productivity in southern terrestrial ecosystems favor greater rates of nitrogen uptake in vegetation, and therefore a lesser role for nitrate in ecosystem acidification (all other factors being equal) in the south with some notable exceptions such as the Fernow Experimental Forest, West Virginia and the Great Smoky Mountains (Nodvin et al. 1995; Peterjohn et al. 1996). The result of these differences is that ecosystem acidification tends to be more greatly affected by the extent of soil sulfate adsorption in the Mid-Atlantic and southeast than in the northeast of North America, and episodic acidification tends to be more strongly driven by sulfate in the south than in the north. There are some exceptions to this generalization such as the high rates of sulfate-driven episodic acidification after droughts that have been identified in watersheds that contain large amounts of wetland area in southeast Canada (Eimers et al. 2007). Additionally, the recovery of acidified ecosystems in the Mid-Atlantic and southeast United States appears to be slower because of the large existing pool of adsorbed sulfate, much of which is strongly retained and bleeds out quite slowly, carrying with it the acidifying H^+ ion (Turner and Kramer 1992; Sullivan et al. 2004; Webb et al. 2004).

One of the first studies linking acidification to atmospheric sulfuric acid deposition as a major source of stress in North American aquatic ecosystems was by Beamish and Harvey (1972) who related fish kills in central Ontario to increases in lake water acidity. Subsequent research showed that as the pH of surface waters decreased below 6, many aquatic species including fish, invertebrates, zooplankton, and diatoms, tended to decline (Schindler 1988). Additional pH decreases to values below 5.3, typically resulted in high concentrations of dissolved inorganic monomeric aluminum, which directly impairs many aquatic organisms. For example, studies of trout found that acidification and associated aluminum interfered with proper osmoregulatory functioning of the gills, and decreased the hatching success of eggs and the survival of fry (Driscoll et al. 1980; Baker and Schofield 1982).

Another effect of acidification on aquatic ecosystems was to sharply reduce biodiversity, particularly at pH values <5. Significant fish population reductions and loss of biodiversity driven by acid deposition have been identified in Nova Scotia (Watt et al. 1983), Ontario (Beamish and Harvey 1972), the Adirondacks and Catskills of New York (Baker et al. 1993), the Upper Midwest of the United States (Schindler et al. 1989), New England and Pennsylvania (Haines and Baker 1986), and Virginia (Bulger et al. 2000). Researchers have also identified deleterious effects on fish species by short-term episodic acidification driven by rain events and snowmelt (Stallsmith et al. 1996; Baldigo and Murdoch 1997).

Though changes in fish populations are perhaps the most obvious and widely reported effects of acidification on freshwater ecosystems, losses of many other aquatic organisms has also been documented. For example, acidification decreased species diversity of diatom algae in a predictable manner, and therefore, analyses of lake sediment cores can be used to infer the historical pH of lakes (Sullivan et al. 1990). Zooplankton and benthic invertebrate communities are also negatively impacted by acidification, causing major disturbances to the lower part of the food web (Allard and Moreau 1987; Havens et al. 1993; Rosemond et al. 1992; Smol et al. 1998; Havas and Rosseland 1995). Mayflies for example, are particularly sensitive to acidification, and the abundance of many species declines rapidly and markedly at pH <6 (Raddum and Fjelheim 1984).

Comprehensive estimates of the amount of aquatic habitat that has been affected by or depleted of species due to acidification is difficult because of the large and varying number of species that can be present, and the role of other disturbance factors such as forestry, agriculture, urban expansion and climate change. However, Schindler et al. (1989) estimated that 23% of lakes in the northeastern United States had "pH values reduced to levels that are no longer suitable for many of the species that were originally important in the food webs of eastern lakes". In some regions such as the southwestern Adirondack Mountains of New York, estimates are even higher, with as much as 30–45% of lakes with pH <6.0 having undergone large historic decreases in pH and ANC (Cumming et al. 1992). Estimates of acidified aquatic habitat (ANC <20 μeq L^{-1}) are in the range of about 8–25% for the Appalachian Plateau, Valley and Ridge, and Blue Ridge Provinces (Sullivan et al. 2007a). In the Atlantic Provinces of Canada, over 50% of lakes have alkalinity levels lower than 40 μeq L^{-1}, a level known to increase acid stress, while Ontario and Quebec have between 20 and 25% of lakes with this sensitivity level (Jeffries et al. 2004). It is important to note that historical ANC values may have always been low (<50 μeq L^{-1}) in many lakes and streams that currently have low values (Chen and Driscoll 2004); the pH values and aluminum concentrations in such waters may have never been suitable for aquatic species considered part of typical regional aquatic food webs.

Acidification of surface waters has had measurable impacts on regional fish populations. In the Adirondack Mountains of New York, about 16–19% of the lakes lost one or more fish species between the 1930s and 1980s (Baker et al. 1993). In Nova Scotia, Watt et al. (2000) reported that Atlantic salmon were extirpated from 14 rivers, and severely impacted in a further 20 due to acidification. Similar proportions of aquatic habitat were impacted in other locations such as the LaCloche Mountains of Ontario (Harvey 1975). Although currently less impacted by acidification than those in the east, high elevation lakes in the Rocky Mountains and the Sierra Nevada Mountains have little ability to buffer inputs of acid deposition (Eilers et al. 1989; Campbell et al. 2004a). With continued population growth upwind of these mountain ranges, future acidification of western watersheds may well follow past patterns of the east. Overall, the impact of acidification is impoverishment of the biotic community that can be sufficient to render the remaining aquatic community less stable and less resistant to other stresses (Schindler et al. 1989).

A relatively recent topic of research is the effects of acid deposition-driven soil acidification and low calcium availability on the reproductive success and fitness of aquatic biofauna (Jesiorski et al. 2008) and a variety of songbirds including Wood Thrush, Tree Swallows, Black Chickadees, and others (Mahony et al. 1997; Hames et al. 2002; Dawson and Bidwell 2005). The principal stressor appears to be low calcium availability exacerbated by acid deposition-driven soil mineral depletion, but several other factors such as forest fragmentation likely play a synergistic role in these bird effects (Hames et al. 2006). Low soil calcium availability results in low biomass of calcium-rich invertebrate prey species such as snails, millipedes, pill bugs, and slugs (Graveland et al. 1994). These changes can result in the inability of these bird species to sequester enough calcium from their typical diet to successfully lay a clutch of eggs, and raise the chicks to the fledgling stage (Graveland 1996). Overall, the conclusion of numerous studies is that calcium availability can limit the fitness of several songbird species. However, none of the published studies has directly linked bird effects to acid-precipitation driven acidification, although a recent study has demonstrated through a controlled experiment that Ovenbird and snail abundance increased with liming in an acidified region of Pennsylvania (Pabian and Brittingham 2007).

The direct toxicological effects of atmospheric sulfur deposition on plant ecosystems are not as clearly understood as the effects described previously for aquatic ecosystems. Progress has been hampered by the long response time of trees to environmental stresses as well as a myriad of other factors that can affect forested ecosystems (Driscoll et al. 2001). However, fog and cloud water intercepted by the forest canopy can be acidic enough (pH 3.0–3.5) to directly erode plant leaf surfaces (Schemenauer 1986; Cox et al. 1990), reducing their resistance to pathogenic fungi. The fog acidity can also leach calcium from leaf cell membranes reducing frost hardiness and inducing tree decline (DeHayes et al. 1999; Lazarus et al. 2004).

Other work from Mexico suggests that the direct action of acidic rain can corrode leaf surfaces, causes bark peeling and increases the acidity levels of wood (Savedra-Romero et al. 2003; Calva et al. 1995).

Progress in better understanding the effects of acid deposition on forested ecosystems was slowed during the 1980s and 1990s in part by a long-standing debate in the scientific community as to whether or not atmospheric deposition significantly accelerated the leaching loss of exchangeable base cations and the acidification of soils (Johnson et al. 1991). Soil acidification and slow loss of exchangeable soil base cations is a natural process in the presence of aggrading forest vegetation. However, more recent studies from a wide variety of regions in North America have shown that both vegetation accumulation as well as acid deposition contribute significantly to base cation losses (Knoepp and Swank 1994; Johnson and Todd 1990; Likens et al. 1996; Houle et al. 1997).

A number of other factors can also contribute to soil base cation losses, including: decreases in atmospheric base cation deposition (Hedin et al. 1994), forest harvesting and associated wood removal (Federer et al. 1989), and nitrogen fixation (Van Miegroet and Cole 1985). Three of the four base cations, calcium, magnesium, and potassium, are important nutrients needed for tree growth and health, and the exchangeable soil pool is a readily available source of these nutrients.

Further contributing to uncertainty about the role of acid deposition in base cation depletion was that some studies were unable to document long-term losses in soil exchangeable base cations in regions where these losses would be expected to occur given past rates of acid deposition (Johnson et al. 1994; Yanai et al. 1999). However, several new methods have more recently been applied to evaluate the rates of base cation depletion from forest soils and have resulted in greater acceptance of widespread depletion in acid sensitive regions of North America (Bailey et al. 2003; Bullen and Bailey 2005; Bailey et al. 2005; Courchesne et al. 2005).

A large number of soil studies from regions in North America sensitive to aquatic acidification have now shown widespread base cation depletion for which acid deposition is believed to be the primary cause (Likens et al. 1996; Hyman et al. 1998; Lawrence et al. 1999; Huntington et al. 2000; Watmough et al. 2005). Base cation depletion is important not only for its effects on surface water chemistry, but also because low base cation availability can affect numerous species in terrestrial and aquatic ecosystems (Jeziorski et al. 2008).

The role of low soil calcium availability was first recognized in the 1980s as a potential contributing factor to freezing injury that is responsible for red spruce dieback in montane ecosystems of southeastern and northeastern North America (Joslin et al. 1992; McLaughlin et al. 1992). Loss of base cations reduces forest growth, regeneration and productivity depending on site characteristics (Juice et al. 2006; Ouimet et al. 2006; Schaberg et al. 2006). Effects on red spruce include increased susceptibility to winter injury, increased crown dieback, and increased proliferation of insects and diseases. These effects may reduce forest growth and increase mortality and over time, the accumulation of health problems will reduce stand productivity and lead to shifts in forest species composition and diversity (Schaberg et al. 2006).

Acid deposition and associated depletion of exchangeable calcium and magnesium in soils has been implicated as a cause of widespread sugar maple decline in regions such as the Allegheny Plateau of Pennsylvania and in southern Quebec (Horsley et al. 2000; Duchesne et al. 2002; Bailey et al. 2004; Minocha and Richardson 2006). Many studies have also shown that high levels of soil manganese and aluminum released under acidic conditions also are associated with sugar maple decline (Horsley et al. 2000; Hallett et al. 2006; Kogelmann and Sharpe 2006). There are also indications that sugar maple may be showing more subtle decline as evidenced by slowing growth rates across broad areas of acidification-susceptible landscapes of northeastern North America (Duchesne et al. 2002; Hallett et al. 2006; Schaberg et al. 2006), although other factors unrelated to acid deposition such as soil moisture from climate change and beech bark disease are also potential causes of sugar maple decline in some areas (Horsley et al. 2002; Hane 2003). The role of base cation availability in sugar maple decline is also supported by a study showing that liming increases tree vigor and crown density in declining stands on the Allegheny Plateau (Long et al. 1997).

Effects of acid deposition on soil calcium have also been demonstrated in Mexico. In Veracruz State, three gas processing facilities emit 5381.9 g s^{-1} of SO_2 (Bravo et al. 1985), and in the vicinity of these facilities, Mora-Palomino (2005) measured a daily dry deposition of 100–117 μg SO_2 m^{-2}. Siebe et al. (2001) studied the soils along a 12 km transect downwind of the facility, and observed a small decrease in soil pH, but a loss of exchangeable Ca and Mg, paralleled by an increase in soil sulfate and exchangeable Al concentrations. They mapped the affected area around one facility by measuring the Ca/Al ratio in the upper 20 cm of the soils, and found that 4 ha were severely impacted and another 1500 ha moderately impacted by acid deposition.

Another calcium-related effect of acid deposition is the accelerated corrosion of buildings and monuments surfaces. Many studies throughout North America have demonstrated effects on marble and bronze surfaces (see references cited by Bricker and Rice 1993). This problem is heightened in Mexico due to the many ancient marble structures built by the Mayan civilization. Bravo et al. (2000) measured the pH, conductivity, and ionic content of precipitation samples near the Tulum archeological site in Yucatan, and found that 45% of the samples were acidic ($pH<5$) in 1994 and 1995. Limestone samples from Tulum showed significant losses of calcium under local acid deposition conditions when irrigated with artificial acid precipitation in a simulated rainfall chamber (Bravo et al. 2006). El Tajin, another archeological site near the Gulf of Mexico, is also affected by acid rain (pH range from 4.3 to 4.5), and experiments showed that the surfaces of the historic limestone monuments there were dissolved by acid rain (Bravo et al. 2003). Using a variety of meteorological data, the origin of acid precursor emissions at the El Tajin site was determined to be an active oil platform in the Bay of Campeche, about 500 km upwind (Kahl et al. 2007; Parungo et al. 1990).

6.1.3 Effects of Atmospheric Nitrogen Deposition

In the 1970s and early 1980s, sulfate was viewed as the major driver of ecosystem acidification because approximately two thirds of the strong acidity in acid rain originated from sulfuric acid and sulfate was the major anion present in most surface waters. This view began to be modified with the recognition that atmospheric nitrogen deposition in the form of nitrate (NO_3^-) and ammonium (NH_4^+—which rapidly oxidizes to NO_3^- in oxigenated soils and waters) was in excess of ecosystem assimilation capacity across parts of North America and Europe (Aber et al. 1989). Additional work in the 1990s also indicated that short-term episodic acidification of surface waters during snowmelt and rain events was largely driven by nitrate in northeastern North America and not sulfate (Murdoch and Stoddard 1992). By the mid- to late-1980s, the concept of nitrogen saturation was introduced (Nihlgaard 1985; Skeffington and Wilson 1988), which explained observations that many regions in Europe were receiving nitrogen from the atmosphere in excess of the ecosystem capacity for uptake, resulting in nitrate leaching to surface waters.

Aber et al. (1989) hypothesized a series of nitrogen saturation stages whereby progressive changes in rates of ecosystem processes should be observed. Stoddard (1994) later linked these stages to nitrate leaching patterns in surface waters. One impact of this work was that ecosystem acidification began to be treated more formally as a multipollutant problem by the 1990s, rather than as mostly a sulfur-driven. In addition to acidification, elevated rates of nitrogen cycling induced by atmospheric nitrogen deposition are known to alter the species composition and diversity of terrestrial and aquatic ecosystems, and contribute to eutrophication, especially in estuaries.

Deposition of the major air pollutants, acidity, ozone and nitrogen to forested ecosystems all tend to increase plant shoot to root biomass ratios, either by inhibiting root development, by changing carbon allocation patterns, or by increasing soil toxicity through increases in aluminum availability in soils. Inorganic nitrogen deposition may also stimulate canopy growth by foliar uptake and by-passing the root periodicity controls of excessive nitrogen uptake (Aber et al. 2003). The accumulative disproportion of root to shoot biomass ratio are likely causes of rapid declines in affected forest trees promoted by extreme weather events that further injure roots (extended winter thaw) or are exacerbated by drought.

The impact of atmospheric nitrogen deposition is not well understood in arid land ecosystems where soils are typically low in available nitrogen. In the northern Chihuahua desert of Central New Mexico in the United States, nitrogen deposition increased at an annual rate of 0.049 Kg ha^{-1} $year^{-1}$ between 1989 and 2004. Analysis of data suggested that continued atmospheric nitrogen inputs were likely to increase grass cover, decrease legume abundance, and could favor blue grama at the expense of the current dominant species black grama (Baez et al. 2007).

A large number of studies have explored the effects of atmospheric nitrogen deposition on terrestrial and aquatic ecosystems of the Rocky Mountain region of North America. The highest rates of nitrogen deposition within this region and the most acute effects are in the Front Range of Colorado and Wyoming, east of the Continental Divide. Here, atmospheric nitrogen deposition ranges from 4 to 7 kg nitrogen ha^{-1} $year^{-1}$ at high elevations, and decreases markedly to the west and with decreasing elevation (Burns 2003). High elevation ecosystems in this region show symptoms of nitrogen saturation such as low watershed nitrogen retention, alteration of alpine plant communities, and changes in the species composition of diatoms in alpine lakes that are comparable to the extent of nitrogen saturation effects documented in mountainous regions of eastern North America that receive about twice as much atmospheric nitrogen deposition (Wolfe et al. 2003; Burns 2004; Bowman et al. 2006). The short growing season, sparse vegetation, thin soil, abundant exposed bedrock, and cold, harsh, snow-dominated climate contribute to the lower threshold of nitrogen saturation in the Rockies compared to that of humid regions. Recent work at Loch Vale, Colorado indicates that the amount of atmospheric nitrogen deposition sufficient to produce aquatic ecological change due to eutrophication (also called the critical load) is 1.5 kg nitrogen ha^{-1} $year^{-1}$, much lower than values suggested for northeastern North America (Baron 2006).

Eutrophication and hypoxia are widespread in estuaries throughout North America including Long Island Sound, the Chesapeake Bay, and the Gulf of Mexico near the Mississippi River Delta (Diaz 2001). Nitrogen is usually limiting to algal productivity in coastal marine estuarine ecosystems, so that nutrient enrichment and hypoxia in estuaries has often been attributed to riverine nitrogen. The relative role of atmospheric deposition as a source of nitrogen to coastal estuaries can vary widely from about 10% in the Gulf of Mexico/Mississippi Delta region, to 25% in the Chesapeake Bay, and to more than two-thirds in coastal river estuaries of northern New England (McIsaac et al. 2001; Boyer et al. 2002; Sheeder et al. 2002). The relative contribution of nitrate and ammonium to atmospheric nitrogen deposition in estuarine watersheds also varies widely. Although nitrate is generally the dominant form of inorganic nitrogen deposition in most North American locations, ammonium can be the dominant form in parts of estuarine watersheds, and is strongly related to agricultural land use (Lawrence et al. 2000; Whitall et al. 2003).

6.1.4 Ozone and Terrestrial Ecosystems

Over the past 50 years, a large volume of literature has documented the effects of ozone on forest trees in the United States (also Chap. 12). Karnosky et al. (2007a) recently provided a 50-year retrospective view of ozone and forests in the United States. First was the discovery during the 1940s–1960s of the phytotoxicity of ozone to forest trees. Later, shifts in plant populations related to ozone were demonstrated in North American forest trees. This observation was followed by the demonstration that ambient ozone decreases tree growth and productivity, and that ozone exposure is linked with shifts and plant communities.

Ozone effects are known to cascade through tree gene expression, biochemistry, and physiology, ultimately feeding back to productivity, predisposing trees to pest attack and causing changes in water-use efficiency (Percy et al. 2002, 2009; Karnosky et al. 2003, 2005, 2007b). Because carbon enters trees through leaves via photosynthesis, the impacts of pollutant gases on leaf morphology, chlorophyll content, Rubisco content, stomatal density, stomatal conductance, leaf area in the canopy, and phenology of leaf display play critical roles in carbon budgets of forest trees (Karnosky et al. 2005).

Ozone effects on photosynthesis vary by genotype and leaf age. Average maximal photosynthesis can be depressed by 29–40%, depending on genotype, and older leaves tend to be more severely affected than younger ones. Ozone can decrease chloroplast size, starch content, mesophyll cell wall thickness, and alter foliar ultrastructure. Ozone can have major negative impacts on both leaf area index (LAI) and leaf display duration. LAI can be significantly decreased under elevated ozone throughout the growing season due to several factors. First, bud break is delayed so that leaf out is later in the spring; secondly, leaf senescence and leaf abscission are accelerated under elevated ozone. Accelerated leaf aging is a well-documented phenomenon associated with ozone. Ozone also induces visible foliar symptoms, decreased leaf retention, altered epicuticular wax chemistry and structure, decreased photosynthesis and increased stomatal conductance in the ozone-sensitive genotypes. In controlled studies, ozone exposure has been shown to decrease aspen productivity by about 23–29% (Karnosky et al. 1996; King et al. 2005).

New research by McLaughlin et al. (2007) in eastern Tennessee near Great Smoky Mountains National Park has shown that ambient ozone episodically increased the rate of water use and limited growth of mature trees within the study region. Stem growth loss was 30–50% less in a high- ozone year, and ozone was suggested to amplify the adverse effects of increasing temperatures on forest growth and forest hydrology (McLaughlin et al. 2007). Ambient ozone levels can also induce visible foliar injury in sensitive herbaceous species (Souza et al. 2006), alter community composition (Barbo et al. 1998) and affect reproduction (Chappelka 2002). As with tree species, whole-plant response to ambient ozone in herbaceous species, such as coneflowers growing in Great Smoky Mountains National Park, is a “complex of independently varying attributes that result in varying degrees of sensitivity among individual plants” (Grulke et al. 2007). Within the wider context of linking ozone impacts to nutritive quality of natural plant communities, there is new evidence that exposure to elevated levels of ozone reduces the digestibility of clover, and that co-exposure to elevated levels of CO_2 does not offset the negative effect of ozone on nutritive quality (Muntifering et al. 2006).

The effects of ozone exposure on plants have also been documented in Mexico. Biomarkers of ozone exposure were investigated at macroscopic and microscopic levels in *Abies religiosa* (Sacred fir) from Desierto de los Leones in central Mexico (Alvarez et al. 1998). One of the most obvious effects of the ozone on plants was chlorosis and necrosis initially expressed as discrete lesions scattered over the needles. This was followed by premature scenescence and loss of the needle, reduced tree growth and vigor, predisposition to bark beetles and tree death (Alvarez et al. 1998). Recent Mexican investigations have also indicated that indirect effects such as limited root colonization by symbiotic fungi on ozone-damaged *Pinus hartwegii* trees is occurring leading to a reduction of the natural regeneration of this species (Bauer and Hernadez 2007).

6.1.5 Role of Mercury and Other Metals

Mercury is a metal that is readily transported long distances in the atmosphere and is deposited to ecosystems in precipitation, either as gaseous, or particulate bound form. Mercury is of environmental concern because it acts as a powerful neurotoxin; its effects are subtle at low levels, but can be fatal to humans and animals beyond certain threshold levels. Several well-documented, localized environmental catastrophes such as in Minamata, Japan in the 1950s (Harada 1995) and in rural Iraq in the early 1970s (Bakir et al. 1973) have demonstrated the toxicity and widespread human health effects of mercury poisoning at high concentrations. In elemental or ionic forms, mercury is relatively harmless in ecosystems, but when methylated by bacteria, it becomes bioavailable and can be readily biomagnified through food webs (Rudd 1995; Mergler et al. 2007).

There are many examples of localized mercury contamination of ecosystems such as in mining areas, burial or discharge of industrial waste, and near chlor-alkali plants (Wiener and Shields 2000; Domagalski 2001). However, the current discussion will focus on mercury contamination of ecosystems from relatively low levels of mercury atmospheric deposition that may originate from the combined emissions of local, regional, and global sources. These mercury sources are believed to include coal-fired power plants, medical waste incinerators, other industrial emissions, and also include natural emissions from sources such as volcanoes and soils (Seigneur et al. 2004). Data from lake sediments affected by long-range transport generally indicate a 2–5-fold anthropogenic enhancement of mercury deposition relative to pre-industrial times (Lamborg et al. 2002; Biester et al. 2007). Some studies of glacial ice and peat bogs suggest an even greater mercury enhancement of 10-fold or more over shorter time periods (Schuster et al. 2002; Roos-Barraclough et al. 2006). In most global and North American locations, mercury deposition appears to have peaked between the 1960s and 1970s and has been declining since (Engstrom and Swain 1997; Kamman and Engstrom 2002; Slemr et al. 2003), with some recently noted exceptions (Bookman et al. 2008; Monson 2009). In some remote locations such as Alaska and northern Canada, mercury deposition levels are either stable or may still be increasing (Braune et al. 2007; see also Chap. 12).

Mercury has three principal operationally-defined forms in the atmosphere that include gaseous elemental mercury (GEM), reactive gaseous mercury (RGM-in the oxidized +2 form), and particle bound mercury in various forms. Mercury in the GEM form is relatively less reactive and has an atmospheric residence time in the range of one year compared to the more reactive RGM and particle bound forms with much shorter residence times and a greater tendency to be deposited to earth's surface (Lindberg et al. 2007). Because of the vastly different residence times and deposition tendency of these various forms of mercury in the atmosphere, redox reactions that control the movement between different forms are key to understanding mercury deposition. As of the 1990s, oxidation of GEM by ozone was the only major set of identified reactions, but more recently, reactions with OH, Br, BrO, and Cl_2 have also been identified (Lindberg et al. 2007).

These various forms of mercury are deposited to land surfaces as wet and dry deposition. It is important to note that after being deposited to land surfaces, mercury can later be emitted back to the atmosphere, especially as GEM, through a variety of abiotic and biotic mechanisms and interactions with vegetation, soil, and water (Lindberg et al. 2007). Early estimates of atmospheric mercury deposition based on models assumed that dry deposition of mercury was negligible or balanced by emissions from land and water surfaces (Bullock et al. 1997; Pai et al. 1999). However, other field-based studies that have used data from wet deposition collectors combined with measurements of throughfall, litterfall, and/or collection of gaseous and particulate forms of mercury have generally estimated dry fluxes on the order of 60–80% of total mercury deposition to forested ecosystems (Johnson and Lindberg 1995; St. Louis 2001). Progress in better quantifying atmospheric fluxes of mercury to ecosystems has been hampered by a lack of detailed knowledge of the chemical composition of RGM, the lack of sites where all forms of mercury deposition are measured, and a lack of measurements of the balance between smokestack emissions and those from natural surfaces, which reflect a mixture of naturally derived and historically deposited mercury (Pirrone et al. 2008). Recent studies however, are improving estimates of many facets of mercury emissions and sinks in the environment (Gustin et al. 2008).

New field-based studies suggest that dry deposition of mercury may be underestimated by many mercury models (Gustin and Lindberg 2005), although recent model results seem to be converging with field-based measurements (Selin and Jacob 2008). Dry fluxes of mercury are most likely greatest in forest canopies with high leaf area indices (Miller et al. 2005), and relatively high in arid settings where wet deposition is low (Caldwell et al. 2006), but may also be quite high locally near major anthropogenic and natural sources of mercury emissions (Evers et al. 2007). Mercury concentrations in leaves and needles, and the resulting flux to soils via litterfall are believed to represent largely “new” mercury that enters tissue from the atmosphere as mercury (St. Louis et al. 2001; Bushey et al. 2008), with little contribution from either uptake via roots (Bishop et al. 1998) or uptake of mercury from recycled mercury within the ecosystem (Rea et al. 2002). Nevertheless, some newer studies have suggested that soil evasion could be an important source of mercury to foliage (Bushey et al. 2008; Gustin et al. 2002). Currently, estimates of annual dry deposition of mercury to ecosystems have fairly high uncertainty on the order of two-fold or more, because measurements are still scarce, and many uncertainties about sources, forms, deposition velocities as well as the role of soil evasion remain (Driscoll et al. 2007a). In contrast, mercury in wet deposition is fairly well characterized by growing networks of precipitation samplers such as the Mercury Deposition Network in the United States (Fig. 6.2; http://nadp.sws.uiuc.edu/mdn/), and CAPMoN in Canada.

Mercury contamination of ecosystems is widespread in North America. In the United States for example, mercury was responsible for 80% of all state fish consumption advisories in 2006, and all 50 states plus several territories currently have advisories attributed to mercury (http://www.epa.gov/waterscience/fish/). The recommended fish consumption limits are determined on a state-by-state basis in the

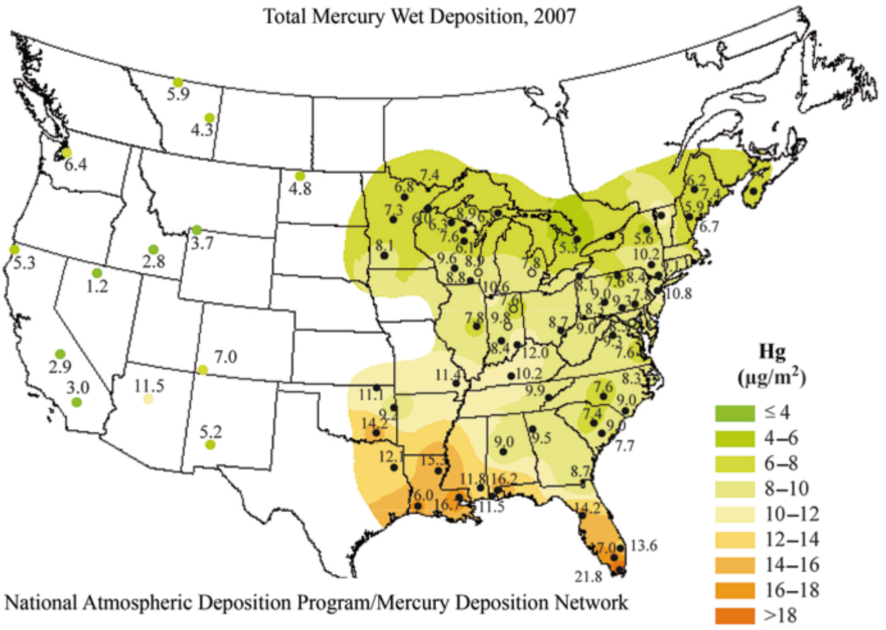


Fig. 6.2 Wet deposition of mercury in the United States for 2007 as determined by the Mercury Deposition Network. (MDN; NADP 2009)

United States, and vary as function of population group risk, body weight, and are often listed on a meals per month basis; typical concentrations that result in a not-to-exceed one fish meal per month warning are in the range of about 0.5–1.0 ppm (http://www.epa.gov/waterscience/fish/advice/mercupd.pdf). In Canada, advisories also are in effect in all 10 southern provinces and in select locations in the Northern Territories (http://www.ec.gc.ca/MERCURY/EN/efca.cfm#NU).

There is a challenge in making generalizations about fish mercury concentrations in the United States and in Canada, because sampling and analysis are the responsibility of each state and province, and methodologies vary widely. However, the conclusion that mercury concentrations in top level predator fish commonly exceed 0.5 ppm in some fresh waters throughout the United States is robust and supported by data from published studies (Kamman et al. 2005; see references cited by Munthe et al. 2007). Data from the National Health and Nutrition Examination Survey (NHANES) sponsored by the U.S. Centers for Disease Control (CDC) indicate that blood mercury levels in young children and women of child bearing age decreased slightly from 1999–2000 to 2001–2002, though the decline was not statistically significant (Jones et al. 2004). A more recent analysis of these NHANES data for the period 1999–2004 found a decreasing trend in blood mercury levels in women of child-bearing age and attributed the trend largely to a shift of fish species consumption (Mahaffey et al. 2008). A current study by the United States Geological Survey is attempting a fully random survey of fish across all significant

U.S. watersheds, which should lead to more accurate predictions of the extent of mercury contamination for the population of fresh waters. Recent evidence indicates that atmospheric mercury deposition has continued to decline over the past few years in many regions of the United States (Butler et al. 2008), and several studies of fish mercury indicate declines in fish mercury concentrations in parts of the United States and Canada over the past two decades (see references cited in Munthe et al. 2007), although studies in some regions are showing either no trends or even increasing mercury concentrations in fish (Bookman et al. 2008; Monson 2009). In addition to the human health effects of consuming fish contaminated with methyl mercury, bioaccumulation has demonstrated effects on piscivorous birds which consume fish with elevated mercury levels as well as fish-eating mammals (Evers et al. 1998; Scheuhammer et al. 2007). Certain fish species show effects that include toxicity, reproductive impairment, and non-toxic neurological impairment (Evers et al. 1998; Fournier et al. 2002; Scheuhammer et al. 2007).

Elevated mercury concentrations have also been shown in the blood of several insectivorous bird species that feed largely in terrestrial ecosystems suggesting mercury bioaccumulation and biomagnification in terrestrial ecosystems (Rimmer et al. 2005). Few data exist on mercury bioaccumulation in terrestrial ecosystems, suggesting a fertile topic for future research and evnvironmental monitoring efforts. Evidence also shows elevated levels of mercury in many amphibian species and possible links with decline in some species (Bank et al. 2005, 2006).

The key processes controlling the bioaccumulation of methyl mercury in aquatic ecosystems appear to be mercury availability, environmental conditions conducive to methylation, transport of the methylated mercury to the water body, and a food web of sufficient complexity to include top-level predators. Data from some studies show a strong relationship between current levels of atmospheric mercury deposition and bioaccumulation of mercury (Hammerschmidt and Fitzgerald 2006), and are further supported by rapid uptake of aerially applied mercury as in the METAALICUS study in Ontario where fish responded rapidly to changes in mercury application rates (Harris et al. 2007). Other data are less supportive of the primacy of current mercury deposition levels, such as in Maine and Nova Scotia, where among the highest levels of mercury in waters and biota in the northeastern United States and southeastern Canada are found despite levels of atmospheric mercury deposition that are regionally low (Vaidya and Howell 2002). Moreover mercury in fish can vary by more than an order of magnitude in a small region such as Voyageurs National Park in Minnesota despite a regionally uniform rate of atmospheric mercury deposition (Wiener et al. 2006). Together, these studies indicate that the importance of current levels of atmospheric mercury deposition to bioaccumulation patterns can vary from strong to weaker and secondary, and may depend on the juxtaposition of a number of physical and biogeochemical factors that affect mercury transport, storage, and transformations. The widespread pattern of mercury-related fish advisories in North America do not in all cases have a straightforward explanation and suggest that other factors such as sulfate deposition, nutrient concentrations, and landscape features can modify the direct impact of atmospheric mercury deposition.

The presence and abundance of wetlands is one of the key environmental factors affecting methyl mercury contamination (Dennis et al. 2005). Inorganic mercury is strongly adsorbed to organic matter in soils and sediments (St. Louis et al. 1994) where methylation occurs. Further, mercury transport in waters is also controlled at least in part by dissolved and particulate organic matter (Babiarz et al. 1998; Yin and Balogh 2002), which is a principal reason why the presence and abundance of wetlands is strongly associated with bioaccumulation of mercury. Additionally, methylation appears to be largely carried out by sulfate-reducing bacteria that are active in the anaerobic subsurface conditions promoted by wetlands (Ullrich et al. 2001), and studies have suggested that sulfate concentrations alone may exert an important control on mercury bioaccumulation (see further discussion in Sect. 6.3.1 of this chapter). Somewhat surprisingly, bioaccumulation of mercury in fish from waters in nutrient-polluted, eutrophied settings such as urban areas or agricultural areas can sometimes be quite low due to a biodilution effect caused by high biological productivity (D'Itri et al. 1971).

The largest mercury pool globally is contained in soils, whereas in forested ecosystems, the vegetation pool is often second largest (Grigal 2002; Mason and Sheu 2002). Mercury concentrations are typically greatest in the O-horizon soil layer, and are strongly associated with organic matter as discussed above, though total mercury pool sizes may be greater in the mineral soil (Demers et al. 2007). There is still a great deal of uncertainty regarding the residence time and mobility of mercury in the soil and other ecosystem compartments because the presence and chemical form of mercury is controlled by a complex mix of processes such as emission/evasion, complexation and transport in waters by organic matter and inorganic constituents, methylation and demethylation, photoreduction induced by ultra-violet radiation, and biotransfer; these processes all affect the storage, transport, residence time, and toxicity of mercury in ecosystems (Munthe et al. 2007).

Many of the factors that affect the rates of these processes are just beginning to be understood in detail, and others such as demethylation remain uncertain. A study in the Experimental Lakes Area of Ontario known as METAALICUS involved the application of three mercury isotopes to a lake and its surrounding watershed. Results have shown rapid incorporation into fish biomass of mercury added directly to the lake, and little movement of mercury added to the terrestrial and wetlands environments surrounding the lake, confirming a long residence time for terrestrially deposited mercury (Hintelmann et al. 2002; Harris et al. 2007).

Although we have stated above that current atmospheric loading of mercury to ecosystems appears to be only a secondary factor affecting bioaccumulation in some regions, research generally shows that mercury deposition broadly correlates with fish methyl mercury concentrations (Munthe et al. 2007; Evers et al. 2007). This suggests that despite the large mercury pools in soils and wetlands of many ecosystems, the surrounding waters and fish may respond rapidly to changes in levels of mercury deposition. However, the response rate will likely differ based on soils, climate, vegetation, wetlands, and other variables. Recent research indicates there can be a fairly rapid response of fish methyl mercury concentrations to reduced atmospheric loading, but that lake ecosystems in a given region can vary widely in their response to similar changes in atmospheric mercury loads alone (Hrabik and Watras 2002; Madsen and Stern 2007). Given the evidence in some regions of strong correlation between current atmospheric mercury deposition and bioaccumulation in aquatic biota (Hammerschmidt and Fitzgerald 2006; Orihel et al. 2007) combined with evidence for decreased atmospheric mercury deposition since the 1970s and 1980s obtained from lake sediment cores (Perry et al. 2005; Engstrom et al. 2007), decreases in mercury concentrations in fish and other biota over this time period would be expected in such regions, although there are few studies that can be cited, and evidence of a long-term decrease in mercury concentrations in fish is mixed (Madsen and Stern 2007; Monson 2009).

Atmospheric deposition of other metals, such as nickel, copper and cadmium can also have severe ecological impacts in aquatic systems (Hutchinson and Havas 1986). Metals can cause toxicological effects on invertebrates (Wren and Stephenson 1991), as well as on fish (Spry and Wiener 1991). Metals are most toxic in acidic waters, because low pH generally favors the dissolved ionic form which is more easily taken up by biota (Nelson and Campbell 1991). Another metal not transported atmospherically, but made available in a toxic form under acidic conditions is aluminum which is the most common metallic element in rocks. Under low pH conditions, ionic Al binds to fish gills disrupting osmoregulation, which can lead to suffocation (Baker and Schofield 1982).

The atmospheric deposition of metals can also have ecological impacts in terrestrial ecosystems (Hutchinson and Whitby 1977). High concentrations of heavy metals such as zinc, copper, manganese, nickel, cobalt, cadmium, lead, and mercury in soils have an adverse effects on microorganisms and microbial processes, especially with those of mycorrhizal fungi which provide the link between soils and roots (Leyval et al. 1997), leading to problems such as reduced plant growth or mortality. The Sudbury Ontario region is probably the North American location which has been most heavily affected by metal contamination from local smelting and refining operations though major emission reductions have resulted in significant improvements in ecosystem health in this region (Gunn et al. 1995).

In the United States and Canada, lead additives were eliminated from gasoline through federal legislation in the early 1980s, but only in 1990 in Mexico. Lead levels are found to be two to four times higher in forests to the south of Mexico City than to the north, indicating north to south atmospheric transport (Zambrano et al. 2002). Additionally, lead as well as many other trace metals have been detected in tree rings of Pinus and Abies from forests surrounding the Mexico City valley. Some of these metals such as iron and zinc may be correlated with vehicle emissions, but also may be influenced by recent volcanic activity in the region. Other metals such as manganese may be affected by local soil acidity such as in the Desierto de los Leones (Calva et al. 2006). Lichen species in the Mexico Valley have also shown enhanced accumulation of many metals that are transported through the atmosphere from pollutant sources. These include chromium, copper, cobalt, iron, manganese, nickel, lead, and zinc. The deposition patterns of vanadium, arsenic, selenium, cadmium, and lead are substantially influenced by long-range transport from Mexico City, whereas chromium, iron, cobalt, nickel, and copper show deposition patterns that are largely determined by contributions from point sources within Mexico (Aspiazu et al. 2007).

Metal contamination due to atmospheric deposition may have also affected aquatic ecosystems in Mexico, and metal-associated transport can be enhanced by local land use practices. For example, sediments at Lago Verde, a freshwater marsh on the lower slopes of San Martin volcano in Los Tuxtlas, Mexico, and currently the northernmost remnant of the tropical rain forest, show evidence of accelerated erosion rates related to the clearing of large forested areas at Los Tuxtlas and higher accumulation rates of heavier and more magnetic sediments. Recent sediments from Lago Verde were enriched in lead and moderately enriched in cadmium, copper, zinc, and mercury. This lake occupies a relatively pristine, non-industralized basin and therefore, increased metal fluxes are likely related to long distance aeolian transport of trace metals (Ruiz-Fernandez et al. 2007).

6.1.6 *Persistent Organic Pollutants*

Persistent organic pollutants (or POPs) are chemicals with a high persistence and toxicity, a relative insolubility in water, and a strong tendency to concentrate with each step in the food chain such that the top predators often have the highest exposures to these chemicals. The best known of this group are the organochlorine compounds like the polychlorinated biphenyls (or PCBs), the dioxins and furans, DDT, toxaphene, chlordane, dieldrin, lindane, endosulfan, mirex, and others. Many of these chemicals are now restricted under international agreements such as the Stockholm Convention, however their presence still has health and economic impacts on society. For example, in 2006, there were 1,023 consumption advisories in place for PCBs in the United States, with an additional 105 advisories for chlordane, 125 for dioxins and furans, and 84 for DDT, constituting about a quarter of all consumption advisories in the United States (EPA 2007b). Likewise, there are over 1,000 consumption advisories for these same organochlorine chemicals in Canada, constituting about a quarter of all consumption advisories in Canada (IJC 2003). For example, all five of the Laurentian Great Lakes currently have fish consumption advisories for PCBs and dioxins, while three have advisories for chlordane (IJC 2003). These advisories are put in place for areas when fish or meat products contain toxic chemicals at levels unsuitable for human consumption. Despite bans on their production, sites contaminated with PCBs and other organochlorine compounds, continue to leach these chemicals into food chains. In addition, active emissions of dioxins, furans and PCBs are a concern around hazardous waste facilities (e.g., Blais et al. 2003), and the widespread presence of these chemicals frequently causes alerts to the public about eating fish and wildlife (e.g., Hites et al. 2004, Rawn et al. 2008).

In addition to the organochlorine chemicals, several emerging POPs are being used as flame retardants to respond to stricter fire regulations, including the polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and polybrominated biphenyls (PBBs) (Rahman et al. 2001; de Wit 2002; Alaee et al. 2003). For example, PBDEs have shown exponential increases in Great Lake smelt (Chernyak et al. 2005) and are found in mother's milk in Europe, the Middle East and North America (Hooper and McDonald 2000). Currently, North Americans have about 20 times higher PBDE concentrations in their blood than Europeans (Hites 2004). Toxicological assessments of PBDEs show analogous behavior to PCBs in that they induce CYP1A via the Ah receptor (Chen et al. 2001). Recently, two PBDE products penta- and octa-BDE, have been banned in Europe and in some U.S. states, and the major manufacturer of these two products in the United States voluntarily stopped production at the end of 2004 (Renner 2004) but the deca-BDE product remains in production.

Another class of persistent organic pollutants is the perfluoalkyl substances, which consist of the perfluorinated acids (PFAs) and the precursors, which include the fluorotelomer alcohols (FTOHs). The PFAs can be subdivided into the perfluorinated carboxylic acids (PFCAs, including perfluorooctanoic acid or PFOA) and the perfluoroalkyl sulfonic acids (PFSAs, including perfluorooctane sulfonate or PFOS). These fluorinated chemicals have been manufactured for over 50 years, and used primarily as refrigerants, surfactants, polymers, and as constituents of fire retardants, lubricants, adhesives, etc., and production of many of these chemicals has increased steadily since the 1970s (Giesy and Kannan 2001). These chemicals can be very persistent in the environment and have been identified as an emerging priority for the Twenty-first century (e.g. IJC 2006). Human serum contains ng/ml concentrations of several PFAs (Hansen et al. 2001), and several of these chemicals have been shown to accumulate in aquatic organisms (Martin et al. 2004a). Initially, these fluorinated chemicals were thought to be metabolically inert due to the strong covalent carbon-fluorine bonds, but mounting evidence is showing that they are biologically active and cause peroxisomal proliferation, increased lipid metabolizing enzyme activity and changes to other important biochemical pathways (Lau et al. 2007).

Although the chlorinated compounds are the most widely studied POPs, and the brominated and fluorinated chemicals are seen as emerging threats to health and the environment, there are many other POPs about which we know much less. These include compounds used in industrial sealants, solvents, plastics, fragrances, some pharmaceuticals, personal care products, and some pesticides which also meet the criteria for classification as POPs. In a pilot screening, Environment Canada's Domestic Substance List identified 91 'new' POPs, with bioconcentration factors of >5,000, half-lives in sediment of >6 months, and were classed as inherently toxic (http://www.ec.gc.ca/substances/ese/eng/dsl/cat_index.cfm). There is very limited information available on these substances in the scientific literature, so they will not be covered in this review.

One remarkable characteristic feature of many POPs is their ability to concentrate to high levels even in remote areas like the Arctic, far from where they were produced. Whenever a chemical is released to the environment, degradation, mixing, and advection will tend to dilute it over time and space. However, when chemical concentrations become higher in areas far from their sources, it suggests that chemical concentrating processes are occurring. These processes typically fall under two categories: (1) solvent switching; and (2) solvent reduction (Macdonald et al. 2002). Solvent switching occurs when a chemical concentrates in a given phase to achieve thermodynamic equilibrium, such as when a hydrophobic PCB concentrates in a fish's gill because its lipid solubility greatly exceeds its water solubility. Another mechanism for concentrating chemicals is by solvent depletion, which is analogous to distillation in that it occurs when a chemical concentrates because it is dissolved in a medium that is being depleted, such as when a chemical in concentrated in fat reserves during starvation. It also describes the tendency for chemicals to 'biomagnify' in food web when chemicals are efficiently transferred from prey to consumer while energy reserves from food are being consumed.

Specifically, biomagnification is the process whereby chemicals work their way up the food chain by accumulating in the body fat of living organisms, becoming more concentrated as they move from one organism to another. This process of biomagnification is one of the reasons why top food chain consumers in remote places like the Arctic have such high exposures to these chemicals. Many POPs are a major concern in the Arctic because indigenous peoples in the north are amongst the most PCB exposed populations on Earth (CACAR II 2003; Muckle et al. 2001). Indeed, PCB concentrations in umbilical cord serum of Canadian Inuit fetuses showed levels consistent with cognitive deficits reported in other studies (Muckle et al. 2001). Early observations that Inuit mothers in Northern Quebec had 5- fold higher concentrations of PCBs in their milk than southern Canadians (Dewailly et al. 1989) was one of the key factors leading to the development of the Stockholm Convention for Persistent Organic Pollutants in 2004.

Some POPs have considerably more long range transport potential than others. Modeling efforts have attempted to characterize this using the characteristic travel distance (CTD)—defined as the "half-distance" (analogous to a half-life) for a substance present in air or water. These CTDs were calculated using the TaPL3 model, which is designed to assess long range transport potential in a steady-state environment and considers degradation and transport pathways that chemicals may undergo based on their physical-chemical properties (Beyer et al. 2000). CTDs for chemicals discharged into air and water are listed in Table 6.1 and it should be noted that these distances should be assessed relative to one another, because actual distances may vary according to different physical and chemical circumstances.

These long characteristic travel distances help to explain why we see these chemicals distributed globally. Other modeling efforts have endeavored to resolve sources of contamination and transfer of POP's to more remote receptor sites like the Arctic, including the Berkeley-Trent (BETR)-World model, a 25 compartment, geographically explicit fugacity-based model with seasonally variable degradation rates (Toose et al. 2004). Potential for long range transport was assessed based on emissions of contaminants in different regions, combined with the transfer efficiency for a given quantity of chemical from one region of the globe to reach another region. For example, Toose et al. (2004) concluded that Europe and the Orient (in-

Table 6.1 Characteristic travel distances (CTDs, km) for air and water for several POPs listed under the Stockholm Convention. (Source: Beyer et al. 2000)

Chemical	CTD (air)	CTD (water)
Hexachlorobenzene	110,000	2,600
PCB (tetra homolog)	8,900	2,900
p,p'-DDE	2,800	4,300
Toxaphene	2,500	9,700
PCB (hepta homolog)	1,900	2,000
Dieldrin	1,100	12,000
Chlordane	1,000	4,000
p,p'-DDT	830	3,300
2378-TCDD	810	1,300
OCDD	460	1,900
Aldrin	100	1,800

PCB polychlorinated biphenyl, *DDT* dichlorodiphenyltrichloroethane, *DDE* dichlorodiphenyltrichloroethane, *TCDD* tetrachlorodibenzodioxin, *OCDD* octachlorodibenzodioxin

cluding China) have a high potential to contribute αHCH to the Arctic due to their high emission rates, despite having relatively low transfer efficiencies to the Arctic due in part to their orientation in relation to prevailing winds.

Another pathway for POPs to reach remote areas is via migratory animal species, such as anadromous fish and seabirds, which can also be important sources of contaminants to certain ecosystems (Blais et al. 2007). Krümmel et al. (2003) showed that anadromous Pacific Sockeye salmon provided a much more important route of entry than the atmospheric pathway for PCBs to several salmon nursery lakes in Alaska. Sediment PCB concentrations in lakes receiving salmon correlated strongly with sockeye salmon spawning density, suggesting that salmon were the major source of PCBs to lakes receiving high densities of salmon spawners (Krümmel et al. 2003). Gregory-Eaves et al. (2007) further extended these observations by examining contaminant distributions in the food webs of the receiving lakes and observed that PCBs and other POPs in rainbow trout also correlated with salmon spawning densities. The process of contaminant transport and focusing from biological vectors is most pronounced when animals converge following a period of wide dispersal and foraging, such as when anadromous salmon migrate to spawn or when seabirds nest in large colonies (Blais et al. 2007).

There is emerging evidence that the PFAs also have a surprising and unexpected long-range transport potential despite their low volatility. Some of the highest PFA concentrations ever reported in animals were found in polar bears (Martin et al. 2004b), and these have been rising sharply since the early 1990s (Dietz et al. 2008), showing the remarkable capacity for their long range transport and bioaccumulation in remote food chains. Like the organochlorine compounds, the perfluoroalkanecarboxylates and sulfonates are persistent and have biomagnification potential, but they have little or no measurable vapor pressure (Martin et al. 2006). Nevertheless, their presence in remote areas like the Arctic suggests these chemicals follow a more complex atmospheric pathway. It is now thought that some of the PFAs found in the Arctic and other remote areas are derived from the degradation of precursors that are carried by air in the vapor phase, such as the fluorotelomer alcohols (Ellis et al. 2004) and perfluorooctane sulfonamides (Martin et al. 2006), leading to their long-range atmospheric transport.

The most detailed information for toxicity of POPs is from animal studies, where controlled dose experiments have revealed numerous effects from exposure to different POPs, particularly PCBs and PCDD/Fs, including deformities in fetal development, mutations to DNA, immune suppression, neurobehavioral effects, alterations in organs such as the thymus and liver, cancer, and others (Pohjanvirto and Tuomisto 1994). In the field, toxicological effects have also been observed in animals contaminated with POPs, especially in Great Lakes fish eating birds (Grasman et al. 1998). Some of these effects are used as biomarkers, including the induction of cytochrome p450-dependent enzymes, effects on porphyrins, endocrine hormones, and others. Immunosuppression stands out as one of the more sensitive and perhaps environmentally relevant effects of organochlorine compounds on animals (Vos and Luster 1989). For example, immunosuppression was measured in harbor seals (Phoca vitulina) fed Baltic fish and was found to correlate with polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDFs) and planar PCBs expressed as toxic equivalents (TEQs) (De Swart et al. 1995; Ross et al. 1995). In addition, antibody-mediated immunity was suppressed in polar bears at Svalbard when exposed to high PCBs (Bernhoft et al. 2000).

There is considerable epidemiological information on persistent organic pollutants to indicate that POPs have also had toxicological effects on certain human populations. In 1979, children in Yu-Cheng (Taiwan) were exposed to high PCBs and furans in rice bran oil and showed signs of delayed cognitive development and reduced hearing abilities when compared with unexposed children (Chen et al. 1994; Guo et al. 1994). These same children also had more frequent bronchits, upper respiratory infections and ear infections than reference populations (Rogan et al. 1988). In another example, women who ate PCB and dioxin contaminated fish from Lake Michigan had children who scored lower on memory tests, and developed poorer motor skills than children who had lower exposures to these chemicals (Jacobson et al. 1990; Jacobson and Jacobson 1996). In Holland, a study observed that higher prenatal and postnatal exposure to dioxin and PCB was associated with altered immune function at 3 months of age (Weisglas-Kuperus et al. 1995).

Numerous surveys currently underway are showing a widespread distribution of POPs throughout the globe. Recent surveys from the Global Atmosphere Passive Sampling (GAPS) network have revealed the highest air concentrations of POPs in the 10–30°N latitudes (Fig. 6.3), reflecting the high population densities, and possibly the higher temperatures in these areas compared to more temperate regions (Pozo et al. 2009). By contrast, surveys examining POPs in tree bark tend to show highest concentrations of some POPs (e.g. hexachlorobenzene, hexachlorocyclohexanes) in the higher latitudes (>50°N; Simonich and Hites 1995), which is largely attributed to the progressive and gradual transfer of POPs to cooler regions of the globe, also known as 'global distillation' or the 'grasshopper effect'. A progressive movement of PCBs to northern latitudes was also demonstrated in dated lake sedi-

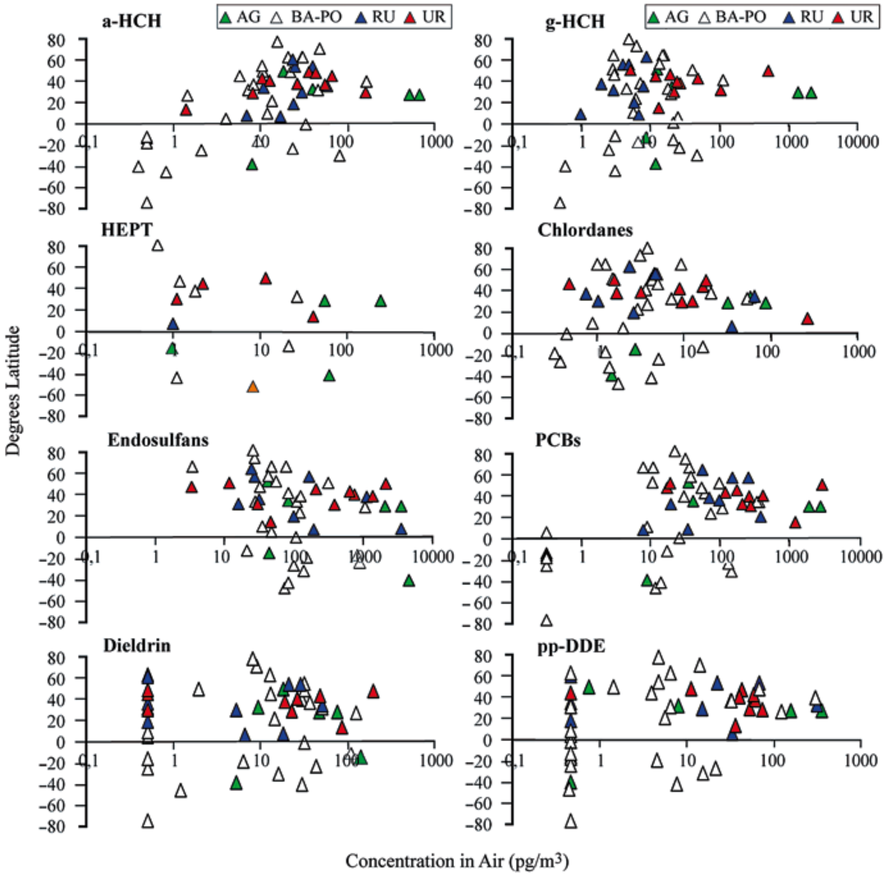


Fig. 6.3 Mean concentrations in air (pg/m^3) of selected POPs collected over four consecutive sampling periods between December 2004 and December 2005 under the GAPS program, arranged according to latitude. (From Pozo et al. 2009)

ment cores (Fig. 6.4), where PCB deposition to sediments in the far north appears to show at least a 20-year lag when compared to more southern latitudes.

6.2 Ecosystem Accountability for Air Pollution Controls

6.2.1 Monitoring

Accountability for assessing air pollution effects on ecosystems is usually accomplished with a combination of data (from field studies that use monitoring or research approaches) and predictive modeling (see also Chap. 12). Monitoring pro-

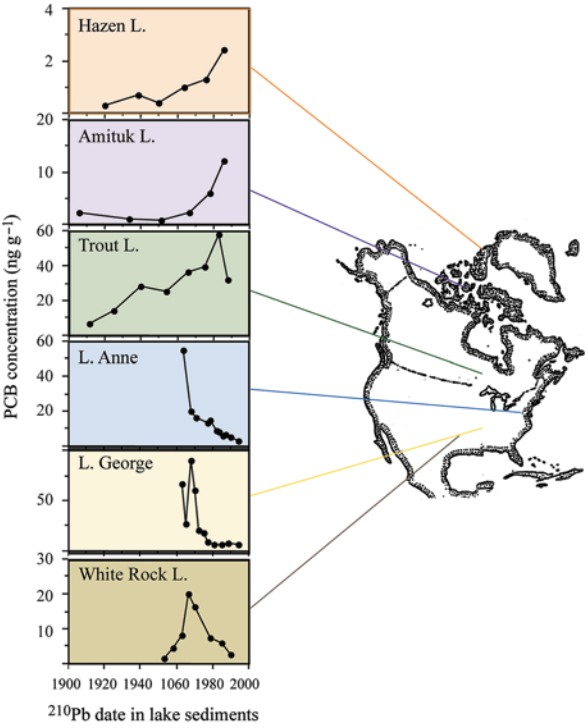


Fig. 6.4 Sediment core profiles of PCBs across a latitude gradient in North America. Note how the northern sites show a lag in the onset and peak of PCB deposition. (Reprinted from Blais and Muir 2001)

grams are designed to assess spatial and/or temporal changes in sensitive or representative ecosystems. Temporal monitoring networks usually need to be long-term in duration (>10 years), while spatial monitoring studies provide an indication of the extent of a problem. Very often, monitoring programs are unable to sustain the funding or institutional support required to maintain a data record long enough to show relevant changes and their causes (Lovett et al. 2007). A number of successful long-term programs do exist that allow an assessment of air-pollutant relevant ecosystem changes, and these are described below.

Another useful, though retrospective, approach for assessing long term trends is the study of cores collected from lake sediment, peat bogs, or glacial ice to assess historical changes to lake and catchment biota and chemistry (Smol et al. 1998). This approach allows a perspective on how ecosystems have changed with historically-documented changes in air pollutant deposition, and thus allows us some idea of pre-stressor conditions. These data are also critical for predictive model calibration.

There are three main complimentary approaches to measuring air pollutant effects in ecosystems. The first is to assess long-term trends in pollutant deposition to ecosystems over long time periods. Examples of these include the atmospheric NADP and CASTNET networks in the United States and CAPMoN in Canada, which have been in operation since the early 1980s.

The second approach is the operation of ecosystem monitoring networks specifically designed to evaluate water chemistry or ecosystem components such as fish or bird populations over large areas. These networks provide assessments of the spatial extent of the problem being monitored. Good examples of these types are regional or national networks that were set up to evaluate the extent of acid rain effects on the chemistry and biota of lakes in Canada and the United States [i.e., the EPA LTM/TIME programs (Fig. 6.5) and the Environment Canada lake monitoring network], as well as networks that assess mercury contamination of fish, which are run in large part by States and Provinces. Conclusions based on data from these monitoring networks can sometimes be extended with data from sites that are not necessarily part of large monitoring networks such as the Hubbard Brook Experimental Forest in New Hampshire, but that collect continuous long-term monitoring data that are relevant to air pollutant effects on ecosystems.

Monitoring networks are usually set-up by government agencies responsible for environmental protection, or industries that are mandated to monitor air pollutant effects on ecosystems. These networks are the first line of accountability in showing the effects of pollution controls on environmental systems. Generally, environmental monitoring networks are designed to address specific issues such as changes in the effect of acid deposition or to assess spatial or temporal trends based on accept-

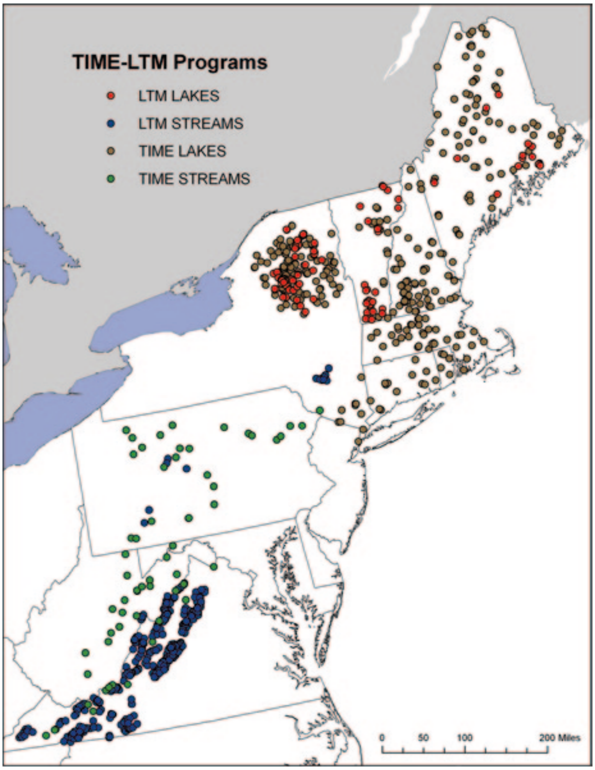


Fig. 6.5 Acid sensitive regions of the northeastern and Midwestern United States with locations of Long-Term Monitoring Program (LTM) and Temporally Integrated Monitoring of Ecosystems locations marked. (From Kahl et al. 2004)

ed statistical approaches allowing stakeholders to determine if pollution controls are having the desired effects on the environment.

The third level of assessment is through research studies in specific regions. These can be carried out in laboratories or in the field (or a combination of both) and are used to understand and quantify geochemical and biological processes which occur in environmentally stressed systems. These intensively sampled sites also provide data suitable for predictive modeling efforts. A large body of research on the effects of atmospheric stressors to ecosystems has been done in calibrated catchments or ecosystem studies where research is often focussed on key ecosystem processes. Experimental applications such as added pollutant loads or liming studies are often done at these intensive research sites to test hypotheses about air pollutant cycling processes. Generally, the data from these sites provide process-level information that allows a clearer understanding of how air pollutants are transferred and transformed as they move between vegetation, soils drainage waters and aquatic biota. Generally, intensively studied sites contain gauged catchments which are sampled frequently for water, soil and vegetation characteristics.

The main study catchment regions in Canada are at Kejimkujik in Nova Scotia, Lac LaFlamme in Quebec, as well as Dorset (east), Turkey Lakes (central) and the Experimental Lakes Area (ELA) in western Ontario, all maintained by government agencies. In the United States, some of the principal study sites are Hubbard Brook, New Hampshire; Sleepers River, Vermont; Bear Brook, Maine; Arbutus Lake in the Adirondack Mountains of New York; Biscuit Brook and several catchments in the Catskill Mountains of New York and in the Appalachian Mountains of Pennsylvania; Fernow in West Virginia; White Oak Run and nearby catchments in Shenandoah National Park, Virginia; Coweeta, North Carolina; Walker Branch near Oak Ridge, Tennessee; Little Rock Lake, Wisconsin; and Green Lakes and Loch Vale in Colorado. Many other smaller research sites are also currently maintained in North America that focus on various aspects of ecosystem pollutant effects. Currently, no similar intensive research sites exist in Mexico.

Many of these sites have detailed data available on soil and water chemical and physical properties and vegetation biomass and nutrient content. Work at many of these sites has provided detailed data on rates of acidification-related processes such as sulfate adsorption, nitrification, and mineral weathering. Most of these sites have long-term data on surface water chemistry that can be used for trend analyses. A weakness of relying on these research sites for monitoring data is that they are not necessarily part of formal networks and receive sporadic funding from a wide variety of sources. As a result, these intensive sites are not necessarily chosen to be representative of a region. Despite these limitations, several investigations have compiled data from a variety of these intensive study sites to make broad-based comparisons of regional base cation dynamics (Watmough et al. 2005), nitrogen budgets across catchments in the northeastern United States (Campbell et al. 2004b), and nitrogen cycling processes across sites in the northeastern United States (Aber et al. 2003).

An important weakness in acidification-related monitoring strategies in North America is a lack of long-term continuously collected data on terrestrial ecosystems; acid deposition related monitoring in the United States and Canada has primarily focused on the chemistry of deposition and surface waters. Acid deposition changes soil chemistry, which in turn can affect tree species such as red spruce and sugar maple as discussed in Sect. 6.2.1. Additionally, nitrogen deposition has demonstrated effects on alpine vegetation in Colorado as well as shrubs in California, also discussed in Sect. 6.2.1. At some study sites such as Niwot Ridge, Colorado, long-term funding by the U.S. National Science Foundation has allowed monitoring of vegetation as well as manipulation experiments. In the United States, the Forest Inventory and Analysis program (FIA) of the U.S. Forest Service has collected data on tree species and growth rates at a large network of thousands of plots. But this program is not focused on monitoring acid deposition effects and in only a few regions and for a limited duration has ancillary data such as soil chemistry been collected in these forested plots. A similar program, the Acid Rain National Early Warning System (ARNEWS), was managed by the Canadian Forestry Service but has since been terminated.

Predicting how ecosystems might change with future changes in air pollutant stressors is most easily done using modeling approaches. Two main approaches used in modeling ecosystem dynamics are statistical and process-based models (see the modeling review by Baker (1989) for an overview). The approach selected usually depends on the complexity of the problem, the availability of data, and how well the system being modeled is understood. In the following sections, we will discuss how changes in atmospheric stressor effects have been studied in North American ecosystems and will discuss the various modeling approaches used to predict how changes in stressors will affect sensitive ecosystem components.

6.2.2 Monitoring the Effects of Atmospheric Stressors

6.2.2.1 Acid Deposition Effects Monitoring

Early attempts at acidification assessment in the 1970s largely involved compiling historical water chemistry and/or fish data in regions such as Nova Scotia, Ontario, New Hampshire, or the Adirondack Mountains, and comparing these data to more recently collected information (Watt et al. 1983; Beamish and Harvey 1972; Schofield 1976; Burns et al. 1981). This work was criticized by some, who felt that historical chemistry data were based on primitive analytical methods that could not be rigorously compared to data derived from more recent analytical methods (Kramer and Tessier 1982).

Later in the 1980s, large-scale surveys of lake and stream chemistry, soils, and biology related to acid deposition were done in eastern Canada and the eastern and western United States to delineate the scale of the problem and to identify regions of concern (Jeffries et al. 1986; Linthurst et al. 1986; Landers et al. 1988; Larsen et al. 1994). This work was notable for using statistically based selection approaches to ensure that sites would be representative of regions of concern. As the acidity of atmospheric deposition has decreased since the 1980s in eastern North America, increasing attention has focused on atmospheric deposition effects in western Canada and the western United States. Base metal smelters in northern Manitoba, oil sand exploitation in northern Alberta, as well as the long-range transport of urban pollution are causing concerns in western Canada and the United States in areas previously believed to be little affected by deposition of air pollutants (Baron et al. 2000).

Regional and nationwide surveys of acid deposition effects have primarily focused on surface-water chemistry (Jeffries et al. 1986; Linthurst et al. 1986; Landers et al. 1988) with some notable exceptions (Baker et al. 1990). In Canada for example, over 10,000 lakes, located mostly east of the Ontario-Manitoba border have been sampled and provide an excellent overview of water chemistry conditions. The most commonly applied indicator of surface-water acidification status has been the acid-neutralizing capacity (ANC), because it is a relatively simple and inexpensive measurement to make, and it integrates the effects of several ionic constituents commonly found in waters. ANC is commonly determined analytically by a Gran titration, but ANC can also be defined as the difference of the sum of base cation concentrations (calcium, magnesium, potassium, and sodium) minus the sum of acid anion concentrations (sulfate, nitrate, and chloride). Despite the widespread preference of many for use of ANC as an acidification status indicator, others argue against the use of measured ANC because the value can be influenced by natural organic acidity (Hemond 1990; Lawrence et al. 2007). Despite such criticism many water chemistry surveys have relied on measured ANC values as the principal means of assessment (Jeffries et al. 1986; Linthurst et al. 1986; Baker et al. 1990; Stoddard et al. 1999).

Some of the early work on acidification assessment also evaluated evidence for changes in aquatic biota, primarily fish populations (Schofield 1976; Harvey 1980; Haines and Baker 1986; Watt et al. 1983; Baker et al. 1990). In many cases evidence of decline in fish populations was evident in regions such as the LaCloche Mountains of Ontario or the Adirondack Mountains of New York, or salmon rivers in Nova Scotia, with the most likely causative factor being acid deposition. Some surveys also evaluated changes in other aquatic communities such as benthic invertebrates (Harvey and McArdle 1986), but overall, little biological data are available from surveys other than fish data, and in many instances factors other than acidification may have played a role in fish community changes (Haines and Baker 1986). Because of the widespread availability of surface water chemical data and few biological data from surveys, attempts have been made to extrapolate biological effects based on known community relations to variables such as pH (Webb et al. 1989; Schindler et al. 1989).

Despite the critical role that soil chemistry plays in the acidification of ground water and surface water, little effort has focused on surveys of soil chemistry in acid deposition assessment efforts. The U.S. Environmental Protection Agency carried out the Direct/Delayed Response Project (DDRP) in the 1980s in which detailed soil surveys were completed for the northeastern United States, Mid-Appalachian region, and southern Blue Ridge Province (Lee et al. 1989). These data were recently re-visited and updated with a new soil survey for the portion of the DDRP study located in the Adirondack Mountains, and a principal conclusion was that the most acid-sensitive watersheds are losing exchangeable base cations despite evidence for limited recovery of surface-water chemistry at many of the same sites (Sullivan et al. 2006). In a few other studies in eastern North America, soil-chemistry surveys in eastern North America that were first completed many decades previously without acid deposition in mind, were re-done, and the conclusions are generally consistent with ongoing soil acidification and base cation depletion (Johnson et al. 1994; Bailey et al. 2005). These results highlight the need for additional soil-chemistry surveys that re-visit older study sites, and also point to a critical lack of widespread soil chemistry data to adequately predict ecosystem recovery from reduced levels of acid deposition.

By the late 1970s, the concept of "sensitivity" to acid deposition effects was being widely used as a means of identifying regions where large numbers of surface water bodies were becoming acidified. Techniques employing geological and soils maps as well as fish surveys were being widely used to identify these sensitive regions (Zimmerman and Harvey 1979; Hendrey et al. 1980; Shilts 1981). This and similar early work confirmed the high sensitivity of regions such as the LaCloche Mountains of Ontario and Adirondack Mountains of New York, but also identified many other regions such as Nova Scotia, the upper midwestern United States, and Florida that contained large numbers of sensitive waters. These early studies laid the groundwork for comprehensive identification of acid-sensitive waters which were later sampled in a representative manner through extensive surface-water chemistry surveys in the United States and Canada (Jeffries et al. 1986; Linthurst et al. 1986).

These surveys allowed estimates of factors such as the percent of waters in a region with values of ANC less than a value considered at risk for acidification or the percent of waters with acid deposition-impacted fisheries. These surveys generally found that acid impact and sensitivity tended to increase as lake and stream watershed area decreased and as elevation increased (Rochelle et al. 1989; DuPont 1992). The proportion of acidified waters in these regions (ANC <0 μeq/L) was generally less than one-third, even in the most heavily impacted regions such as the Adirondack Mountains (Baker et al. 1990), and often less than 10% in moderately impacted regions such as the upper midwestern United States (Linthurst et al. 1986). The percent of sensitive waters with ANC <200 μeq/L, however, was much higher, commonly greater than 75% in many regions (Jeffries et al. 1986). These results indicated that a large number of surface waters were in danger of future acidification if current levels of acid deposition continued or increased. The results of these surveys also allowed early estimates of the financial impact of acid deposition on sensitive ecosystems (Minns and Kelso 1986). These early attempts at evaluating financial impact are generally currently viewed as incomplete because of no attempt to evaluate the financial benefits of ecosystem services. More recent work has evaluated the costs and benefits of the cap and trade program that is part of the Clean Air Act Amendments of 1990, but detailed financial assessments of cost and benefits to ecosystems are difficult to find (Burtraw et al. 2005).

A critical part of monitoring ecosystem response to acid deposition is having an accurate record of atmospheric deposition of acidic pollutants. In the United

States, there are three principal nationwide networks: the National Trends Network (NTN); the Atmospheric Integrated Research Network (AIRMon) operated by the National Atmospheric Deposition Program that monitors wet deposition chemistry at more than 250 sites across the United States (http://nadp.sws.uiuc.edu/, accessed 27 Dec 2007); and the Clean Air Status and Trends Network (CASTNET; http://www.epa.gov/castnet/, accessed 27 Dec 2007) operated by EPA and the National Park Service that monitors dry deposition of sulfur and nitrogen species at more than 80 sites across the United States. In Canada, Environment Canada operates the CAPMoN network of 29 wet and dry deposition sites (http://www.msc.ec.gc.ca/capmon/index_e.cfm) and provides support to a number of Provincial networks. These networks allow estimation of total deposition of sulfur, nitrogen, and acidic substances to sensitive ecosystems throughout the United States and Canada.

There are several known limitations and weaknesses of the current deposition networks, primarily regarding dry deposition. First, dry deposition is difficult to estimate because of the variety of surfaces that are impacted by gas and particles. CASTNET uses the "big leaf" model to make these estimates (Hicks et al. 1985), and the limitations and weaknesses of this model have been described previously (Lovett 1994; Clarke et al. 1997). Second, the CASTNET sites do not monitor several critical pollutants known to contribute to acidic deposition including ammonia and nitrogen dioxide. In summary, if CASTNET data are used to estimate total atmospheric deposition to an ecosystem, an underestimate is likely to result, particularly for nitrogen deposition. The CAPMoN network monitors a greater number of nitrogen species, therefore these data are less likely to underestimate nitrogen deposition to as great an extent as CASTNET. Another source of great uncertainty in deposition calculations can occur in watersheds with a wide range in elevation; an NTN or CAPMoN wet deposition site typically represents one point measurement of precipitation amount, and collectors are often located at the base of watersheds where amounts are likely to be lowest. Again, this source of uncertainty in wet deposition commonly results in an underestimation of actual wet deposition.

Several investigators have addressed deposition uncertainty by developing spatial models of atmospheric deposition that incorporate detailed meteorological data and orographic effects to provide more accurate estimates of atmospheric deposition to ecosystems (Ollinger et al. 1993; Weathers et al. 2006). A weakness of these models is that they provide estimates of spatial deposition only for the given time period used to calibrate the chemical part of the model. Applying these models to estimate current deposition is likely to provide out-of-date estimates of deposition, if the data sets used in the model are more than a few years old; this is particularly true in a period when deposition chemistry is changing over time such as in the past two decades.

Long-term lake, stream and river sampling programs in regions with high sensitivity to acidification began in the early 1980s when the scope of the problem became known and these programs are mostly maintained by federal governments in both Canada and the United States. The networks are usually located in undeveloped, acid-sensitive regions of eastern North America and involve the repeated sampling of lakes and sometime streams and rivers, whose catchment soils, bedrock and forest cover have been characterized (see also Chap. 12).

Currently over 400 lakes are sampled at least annually in eastern Canada by Environment Canada, in an area stretching from Newfoundland, to western Ontario. The principal surface monitoring programs in the United States are funded by EPA, and are known as the Long-Term Monitoring and Temporally Integrated Monitoring of Ecosystems projects, sometimes referred to by a single acronym as LTM/TIME (Kahl et al. 2004). Additionally, the U.S. Geological Survey operates several relevant monitoring networks: (1) the Hydrologic Benchmark Network in the northeastern and western United States that monitors chemistry in five meso-scale basins (Murdoch and Shanley 2006); (2) the Watershed Energy and Biogeochemical Budgets that operates a network of five stream chemistry sites across the United States (Baedecker and Friedman 2003); and (3) a stream chemistry network of 13 sites in the Catskill Mountains of New York (http://ny.cf.er.usgs.gov/nyc/unoono.cfm). There are also surface water chemistry monitoring networks funded at the state or regional level that were designed to address acid deposition effects such as the Virginia brook trout stream network (Webb et al. 2004) and the Adirondack Long-Term Monitoring lakes (Driscoll et al. 2007b).

Surface-water monitoring records that extend over 15–25 years in both countries generally show decreases in dissolved sulfate concentrations, consistent with decreases in SO_2 emissions in upwind source areas and decreases in atmospheric sulfur deposition in monitored regions. There are exceptions to this generalization, however; in the mid-Atlantic and southeast regions of the United States consistent downward trends in surface water sulfate concentrations have not been reported, although some streams have shown declines (Webb et al. 2004; Eshleman et al. 2008).

By the late 1990s, ANC and pH had generally not increased as expected in many of the monitored North American water bodies because base cation (calcium, magnesium, potassium, sodium) were decreasing as rapidly, or more rapidly than the strong acid anions reduction, probably due to long-term base depletion in soils from decades of acid deposition (Stoddard et al. 1999). More recently, increasing trends in ANC and pH consistent with the beginnings of aquatic ecosystem recovery have been widely observed in the northeastern United States and in southeastern Canada (Jeffries et al. 2004; Kahl et al. 2004; de Wit et al. 2007; Driscoll et al. 2007b).

There has also been a marked improvement in the chemistry of lakes in the heavily polluted Sudbury area in Ontario due to the large decreases in regional sulfur and nitrogen deposition that have occurred over the last 25 years (Keller et al. 2007). Another trend pattern of note is that studies in the late 1990s were reporting little evidence of decreasing nitrogen deposition or of decreasing nitrate concentrations in surface waters, whereas more recent studies, have observed decreasing trends in nitrogen deposition and of nitrate in surface waters, though these decreases are much less than those of sulfate (Stoddard et al. 1999; Kahl et al. 2004; Driscoll et al. 2007b).

There are some regions of North America that show countervailing trends to those of the discussion above. First, the Blue Ridge in the southern United States contains many acid-sensitive surface waters; there is some evidence of limited recovery in streams of this region, but the decreases in sulfate concentration have not matched those of waters further to the north, and therefore ANC has changed little since the late 1980s (Kahl et al. 2004; Webb et al. 2004). This lack of recovery is attributed to the large amount of adsorbed sulfur stored in the highly weathered soils of the southeast, which were not glaciated during the Pleistocene (Webb et al. 2004).

The western Rocky Mountains, including part of the Great Plains to the east, and Basin and Range to the west, is a region that is generally showing decreasing trends in sulfate concentrations, and increasing trends in inorganic nitrogen concentrations in wet deposition, a pattern that is driven by increases in both ammonium and nitrate concentrations (Lehmann et al. 2005). Evidence from this region, clearly shows that nitrogen loads have increased since the 1950s (Wolfe et al. 2003), but the evidence is mixed as to whether nitrate concentrations or nitrate loads have increased significantly over the past two decades (Caine 1995; Williams and Tonnessen 2000; Clow et al. 2003; Burns 2004). Data from this region do support a decrease in ANC in many surface waters, especially in the Front Range of Colorado (Caine 1995; Williams and Tonnessen 2000), despite slight decreases in surface water sulfate concentrations (Clow et al. 2003). Although surface waters in the Rockies have generally been viewed as not sensitive to acidification (ANC >0 µeq/L), some headwater streams and ponds do acidify or nearly acidify during snowmelt, and downward trends in ANC evident at some sites may exacerbate this situation (Caine 1995; Williams and Tonnessen 2000; Campbell et al. 2004a). In general, the Rockies cannot be viewed as a region that is showing evidence of recovery as in eastern North America.

Evaluations of recovery trends in aquatic biota in surface waters that are showing increases in pH and ANC have been hampered by a lack of continuously collected biological data from these same waters. Although continuously collected biological data are generally lacking, several studies have re-visited waters where historic data are available that were collected during more acidic conditions. The biological recovery trends in these surface waters (primarily in the northeastern United States and in southeastern Canada) have thus far not paralleled the recovery trends in chemistry (Snucins 2003; Jeffries et al. 2004; Burns et al. 2008a). These results may in part reflect biological time lags that may vary from a few years to more than two decades after chemical recovery or may reflect the limited availability of biological data (Driscoll et al. 2001; Snucins 2003; Frost et al. 2006). A noteable exception to the lack of biological recovery comes from the Sudbury region of north-central Ontario, where large reductions in sulfur deposition have occurred since the 1970s (Gunn and Keller 1990; Keller et al. 2007).

Biological recovery is also likely to vary depending on trophic level, with the most rapid recovery expected at the lowest trophic levels (Findlay 2003), although diatoms show less evidence of improvement than aquatic insects in streams of the Catskill Mountains of New York (Burns et al. 2008a). Studies also show that factors such as dispersal and competition with acid-tolerant species will complicate recovery trajectories. For many waters, a return to pre-acidification species richness and biomass may not be easily achievable, and in some cases may require active intervention in the form of food web manipulations (Snucins and Gunn 2003; Binks et al. 2005).

No evidence to date supports widespread recovery of fish populations, even in lakes downwind from the Sudbury region of Ontario (Snucins et al. 2001), however two recent studies find evidence of the return of brook trout to previously acidic stream sites that have shown slight improvements in pH and ANC (Simonin et al. 2005; Burns et al. 2008a). The studies to date suggest that with allowance for time lags, some human intervention where needed, and with continued declines in the acidity of precipitation, a general recovery trajectory to conditions close to those that pre-dated acidification will be possible in many, but not all surface waters.

Recognition of the link between nitrogen sources and deleterious effects on estuarine ecosystems has resulted in formal policy efforts to reduce nitrogen loads to estuaries such as the Gulf of Mexico, Neuse River, Chesapeake Bay, and Long Island Sound. In the Chesapeake Bay, efforts have been directed at reducing point sources and improving best management agricultural practices. Despite these efforts, little improvement has been observed in Bay water quality, and consideration is being given to strategies for reducing atmospheric nitrogen deposition (Boesch et al. 2001). Recent work in Chesapeake Bay has recognized that vehicles are the dominant source of NO_x emissions (Whitall et al. 2004), and a 2007 workshop of the Science and Technical Advisory Committee to the Chesapeake Bay Program specifically focused on the role of these mobile sources of NO_x in atmospheric nitrogen deposition to the Bay (http://www.chesapeake.org/stac/workshop.html).

As discussed above, acidification effects on Mexican ecosystems mainly affect plants because there are few major freshwaters in this country and these are usually located on bedrock insensitive to acidification. A number of studies have looked at the effects of acidification on plants (e.g. Savedra Romero et al. 2003; Calva et al. 1995; Baez et al. 1986; Garcia et al. 2006), but though these studies have identified existing problems of plant health, there are no recurring monitoring programs to evaluate plant health in relation to acid deposition.

There are also studies in Mexico that demonstrate deleterious effects of air pollutants on agricultural crops. For example, studies have found that the susceptibility to fungal opportunistic pathogens increased in mango plantations located downwind from a thermoelectric power plant and was associated with acid rain and nickel- and vanadium-rich ash exposure that affected the fruit peel. (CFE Report 2003; Siebe et al. 2003). The plant burned sulfur-rich fossil fuels and emitted particles of graphite-like carbon with precipitates of VSO_4- and $NiSO_4$. Close to the source (2–4 km distance) up to 18.5 g/m^2 particles were deposited along with 148 mg vanadium and 39 mg nickel. These metals enter the environment in a mobile form, and are readily taken up by the mango tree leaves. Nevertheless, translocation into the fruits was very small. Sulfur deposition also induced increased sulfate uptake by the trees accompanied by increased potassium uptake to maintain the internal charge balance within the plants. However, the latter produced an antagonism in calcium-uptake. This nutrient is already marginally available in the study region, and the sulfur emissions induced calcium deficiency in some orchards. Since calcium is an important element for cell membrane stability, this deficiency facilitates pathogen infections. Also, the high concentrations of vadadium and nickel deposited on leaves and fruit tissues causes local necroses of the plant tissues and facilitates pathogen infections.

Systematic study of the chemical composition of precipitation in Guanajuato State, one of Mexico's most important agricultural areas, allowed the determination of the contribution of nitrogen in precipitation to soils. The total amount of inorganic nitrogen deposited to soils ranged from 6 to 17 kg/ha, representing 5.7 to 22.8% of the nitrogen applied as urea fertilizer during the growing season (Baez et al. 1989).

Direct foliar nitrogen uptake is known to be an important process in some Mexican forest ecosystems. Under greenhouse conditions, a high potential for foliar uptake of nitrogen as nitrate and ammonium was demonstrated for *Abies religiosa*. Additionally, coniferous forests of the Valley of Mexico receive nitrogen deposition 4–11 times greater than under natural conditions, indicating the importance of investigating the effects of this excess nitrogen deposition on these forests (Chavez Aguilar et al. 2006).

6.2.2.2 Mercury and Other Metals

There are few mercury ecosystem monitoring programs for fish or surface waters in North America though there are a number of data sets that could be used to assess spatial patterns (see also Chap. 12). Many states and provinces in the United States and Canada have monitoring programs for mercury and other metals as well as organic contaminants in fish tissue, and many of these jurisdictions publish reports or post data on web sites (see: http://www.health.state.ny.us/environmental/outdoors/fish/fish.htm). Moreover, the Province of Ontario has a large-scale program where sampling for fish mercury is done on a rotational basis. A weakness in many of these data sets is that there is no uniform sampling or analytical methodology used across jurisdictions, and thus sampling strategies and intensity can very widely. Because of these shortcomings, these data cannot generally be used in a quantitative manner to extrapolate across wide regions of the continent.

The Mercury Deposition Network collects data on mercury in wet deposition at nearly 100 sites across the United States, focused mainly in the east and Midwest. This network was begun in 1995, and is operated by the NADP. There is also an effort within NADP to develop a network for monitoring speciated ambient concentrations and dry deposition of mercury in the United States (http://nadp.sws.uiuc.edu/amn/). Recent work on trend analysis of mercury deposition in the United States indicates that mercury concentrations in wet deposition are declining in the northeastern United States during 1999–2006 (Butler et al. 2008). Also, data from lake sediments generally supports that atmospheric mercury deposition peaked in many regions of the United States and Canada during the 1970s, and has generally been stable or declining since (Kamman and Engstrom 2002; Perry et al. 2005; Engstrom et al. 2007), with some exceptions (Sanders et al. 2008).

Unfortunately, there is no comparable network for mercury in surface waters or in biota. Two recent papers have combined mercury ecosystem data from disparate sources into unified databases that can be used to understand spatial patterns of mercury concentrations in waters and bioaccumulation (Driscoll et al. 2007a; Evers et al. 2007; Munthe et al. 2007). Also, a recent paper outlines a formal strategy for mercury monitoring in the United States (Mason et al. 2005). A source of funding remains the principal obstacle to initiating an ecosystem-based mercury monitoring network in the United States and Canada. Additionally, we are not aware of any existing monitoring networks in Mexico for either mercury or other trace metals.

6.2.2.3 Ground Level Ozone: Monitoring and Impacts

Ambient concentrations of urban ozone or oxidants in North America have been measured since the 1960s. Trends in either 1 h or 8 h maximum ozone concentrations since the 1980s are summarized in Chap. 12. There is general trend downward in concentrations in the United States and Canada, and in the Mexico City valley, with some exceptions (e.g., Fig. 12.1 and Table 12.4).

Spatial assessments across North America have shown that ozone is a pervasive air pollutant that causes direct damage to vegetation in natural areas (Percy and Karnosky 2007). Surface-level ozone threatens forests in both the northern and southern hemispheres (Percy et al. 2002), as well as near urban areas such as Mexico City. Some areas far from pollution sources have nevertheless experienced decreased visibility, increased ozone concentrations and elevated nitrogen deposition. High ozone concentrations have been a major pollution problem in the Mexico City basin for at least 10 years, exceeding the Mexican standard of 110 ppbv (see also Chap. 12).

Despite the improvement in regional ozone concentrations mentioned above, Percy et al. (2007) found that aspen was severely affected by high ozone events in large parts of Canada and the United States (see Fig. 6.6).

The first report on oxidant-induced damage in the Valley of Mexico was presented more than 30 years ago. There is now considerable evidence of ozone pollution in the Desierto de los Leones National Park, 25 km southwest of Mexico City, (Bauer et al. 1985; Bauer and Hernandez 1986; Bauer and Krupa 1990; Alvarado et al. 1993; Skelly et al. 1997), and data from an ozone monitor during 1990 and 1991 displayed frequent violations of the Mexican air quality standard (Bravo and Torres 2002; Miller et al. 2002; SIMAT-RAMA http://www.sma.df.gob.mx/simat/consultas.htm). A 30% decrease in maximum net photosynthesis and 18% chlorophyll b degradation were detected in a forest near Mexico City (Zambrano and Nash 2000). Also in the same region, the epiphitic lichen community was shown to have 47% fewer species, 62% less lichen cover, and a species abundance pattern that revealed a highly disturbed community, compared to control sites. Air quality, mainly high ozone levels, may account for many of the observed differences (Zambrano et al. 2000).

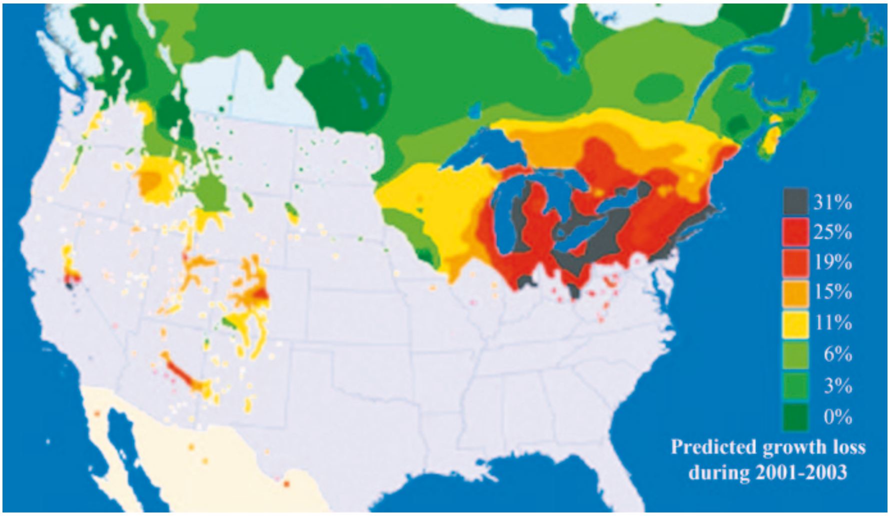


Fig. 6.6 Estimation of aspen growth loss in Canada and the United States. (From Percy et al. 2007)

6.2.2.4 Persistent Organic Pollutants Monitoring

A range of monitoring activities are conducted for POPs in North America, under Article 11 of the Stockholm Convention (http://www.pops.int/document/context_en.pdf). All signatories are to encourage and/or undertake, at national and international levels, appropriate research, development, monitoring and cooperation pertaining to POPs, to their alternatives and to candidate POPs. Notable examples of monitoring activities in North America include the Integrated Atmospheric Deposition Network (IADN) (http://www.epa.gov/glnpo/monitoring/air/iadn.html; see also Chap. 12); the Northern Contaminants Program (NCP) (http://www.ec.gc/media_archive/press/2001/010509–1_b_e.htm), and the Great Lakes Herring Gull Monitoring Program (http://www.on.ec.gc.can/wildlife/fact sheets/fs_herring_gulls_e.html).

IADN was formed in 1990 as a partnership between Environment Canada, the Ontario Ministry of the Environment, and the EPA's Great Lakes National Program Office to monitor POPs in air and precipitation over the five Great Lakes. IADN consists of 5 master stations (one at each of the five Great Lakes) and 10 satellite stations. Air samples are collected for POPs analysis every 12 days at each of the master stations and several of the satellite stations. Precipitation samples are also collected at several sites representing a composite of rainfall over 28 days in the United States and 14 days in Canada.

A number of years ago, monitoring results showed that Great Lake contaminants resulted in impaired health for several waterfowl, including the herring gull, ring-billed gull, double-crested cormorants, and others. To address these concerns, the Great Lakes Herring Gull Monitoring Program began in 1974 to track pollution trends and monitor effects of POPs in waterfowl of the Great Lakes. Problems identified included birth deformities, reduced reproduction, endocrine disruption, and physical deformities. Continued monitoring has shown that many of these problems have improved since the 1980s (EC 1995).

In Canada, the Northern Contaminants Program (NCP) was established by Indian and Northern Affairs Canada in 1991 following reports of elevated human exposure to POPs in animals that constitute the traditional diets of many northern Aboriginal peoples. Reports identified a wide variety of substances reaching unexpectedly high levels in the Arctic environment that were most likely originating from other parts of the globe. Internationally, the Arctic Monitoring and Assessment Programme (AMAP) advises the governments of the 8 Arctic countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Russia, Sweden and the United States) on the status of, and threats to, the Arctic environment. AMAP has published several reports on the status of POPs in the circumpolar Arctic (AMAP 1998, 2004), which includes the results of long-term monitoring of POPs in air, water, and biota. AMAP has also organized human maternal blood monitoring for POPs with data extending back to the early 1990s (http://www.amap.no/).

The Global Atmospheric Passive Sampling (GAPS) Network (GAPS) is a global network consisting of 60 sites on seven continents where concentrations of POPs are measured in air using passive sampling devices that do not require electrical power. The purpose of this network is to investigate concentrations of POPs in the global atmosphere. The target chemicals include legacy POPs listed under the Stockholm Convention such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) as well emerging pollutants—e.g. brominated flame retardants, polyfluorinated chemicals and current-use pesticides (http://www.msc-smc.ec.gc.ca/gaps/).

POPs are also monitored in human populations through the WHO Global Environmental Monitoring System/Food Contamination Monitoring and Assessment programs (GEMS/Food). Eighteen countries participate in this study, where human milk samples from 62 different areas are being analyzed for POPs. Additional studies are being organized by WHO GEMS/Food, which includes the twelve POPs listed under the Stockholm Convention. Other monitoring programs for POPs include the Global Atmospheric Watch program of the World Meteorological Organization, the European Monitoring and Assessment Program, as well as programs administered by the National Oceanic and Atmospheric Association, and the Geological Survey of the United States.

Concentrations of many chlorinated POPs such as those reported by the IADN program over the Great Lakes were dramatically reduced in the 1990s (e.g. Simcik et al. 2000). IADN monitoring of atmospheric PCB concentrations have shown that sites near Lakes Michigan, Erie, and Ontario had relatively higher PCBs than those measured at sites near Lakes Superior and Huron, however PCBs in air over the Great Lakes are reporting declines over time, with half-lives ranging between 7 and 26 years (Sun et al. 2007). Similarly, organochlorine pesticides like HCHs, chlordanes, endosulfans and dieldrin are declining in air over the Great Lakes, reflecting the effectiveness of control measures in these areas (Sun et al. 2006). Some of the brominated flame retardants have also been monitored in air over the Great Lakes by IADN, though this monitoring only began in 2005, thus long term patterns in air are unavailable. Preliminary evidence suggests that some of the PBDE congeners, particularly 47 and 99, are declining in the air in response to recent controls on their production (Venier and Hites 2008).

Interestingly, global patterns of POPs in air seem to paint a somewhat different picture, showing that the legacy POPs still predominate in many instances. Initial results of the GAPS network showed many of the legacy organochlorine compounds were detected throughout the globe including αHCH, chlordanes, dieldrin, and DDT, with some high values that may be related to possible continued use and/or re-emissions from historic use (Pozo et al. 2006). These results have recently been expanded to show that the most prevalent POPs in air were the endosulfans (a current-use organochlorine insecticide) and PCBs. Concentrations of POPs in air tended to be highest at mid-northern latitudes (10°–40°N) throughout the globe, generally reflecting the major historical and current sources of chemical application (Pozo et al. 2009).

Biological monitoring programs have also revealed the effectiveness of control programs on contaminant accumulation in wildlife. For example, monitoring of POPs in archived herring gull eggs from the Great Lakes showed PCBs declining by 75–80% between 1971 and 1982 (Hebert et al. 1999), whereas PBDEs increased in herring gull eggs since the early 1980s with doubling times of 2–3 years (Norstrom et al. 2002). In the Canadian Arctic, monitoring of POPs in Ivory Gull eggs from Seymour Island, NU (Braune et al. 2007), revealed declines since the 1970s for some POPs (DDT, PCDD/Fs), though the rate of decline was much slower than those observed in the Great Lakes. Other POPs (e.g. chlordanes, HCHs) showed no declines since that time (contrary to the pattern observed in the Great Lakes), and still others were shown to increase since the 1970s (e.g. PBDEs). Dramatic increases in long chained PFAs (including PFOS and PFOA) have also been observed between 1975 and 2004 in seabirds from Prince Leopold Island in the Canadian Arctic (Butt et al. 2007). Temporal trends of POPs in polar bear tissue likewise show evidence of slow declines in DDT and HCHs from the 1960s to the 2000s, though other POPs (notably the chlordanes and PCBs) did not show strong evidence of declines over this period (Norstrom 2001). It is clear from these observations that POPs in arctic and temperate regions follow different input pathways and time trends.

Extensive monitoring is in place for existing and candidate POPs throughout the globe in air and biota. Continued support for these programs is needed to track POPs to determine the effectiveness of emissions control programs, as well as to track emerging chemicals. In particular, research into 'new' POPs is required, because there are many emerging POPs about which we know very little.

6.2.3 Predicting Ecosystem Changes with Pollution Management

6.2.3.1 Critical Loads Modeling for Sulfur and Nitrogen Deposition Effects

The data acquired in spatial sampling surveys were initially used to determine which regions were of greatest concern for acidification effects. As our process-level understanding of soil and lake-water chemistry improved, survey data as well as data from intensively-monitored catchments began to be used to assess critical loads for ecosystems potentially affected by acidification as well as by eutrophication. A critical load can be defined as “the quantitative exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur, according to present knowledge” (Nilsson and Grennfelt 1988).

Critical load estimates for sulfur and nitrogen deposition began to be a focus for synthesizing information on atmospheric deposition effects and considering future policy options in Europe, the United States and Canada in the 1980s, however there have been substantial differences in the integration of critical loads into clean air policies among these nations/regions. For example, a critical loads approach was formally adopted in Europe as a guiding principle for air quality management and policy as part of the 1988 Sofia Protocol on the control of nitrogen oxide emissions, and has continued to be employed by the European Union as well as in Canada ever since, under the auspices of the United Nations Economic Commission for Europe (http://www.icpmapping.org/, accessed 4 Jan 2008). The first large scale mapping of critical loads in North America was carried out by Canadian federal and provincial governments (Jeffries et al. 2004), and critical loads continue to be an integral part of air quality policies in Canada.

The situation is different in the United States. Title IV of the Clean Air Act Amendments of 1990 controls acid deposition through a cap and trade emission reduction program under the direction of EPA, which considers but is not formally linked to a critical loads approach. However, other agencies within the United States, such as the National Park Service and the Forest Service each have their own mandates for land management and protection of natural resources that allow the use of critical loads as a management tool, and these agencies are increasingly making use of this approach (Porter et al. 2005). Nonetheless, despite many scientific investigations in the United States that have used critical loads as an ecosystem assessment tool relative to the effects of air pollutant deposition (McNulty et al. 2007; Fisher et al. 2007), the approach has not been used as an enforceable standard as in Europe and Canada (Burns et al. 2008b).

Critical loads can be calculated and applied using either steady-state or dynamic approaches. In the steady-state approach, a snapshot view is made of ecosystem vulnerability to one or more air pollutants. In the case of acidification the amount of acid deposition that will not result in detrimental effects to a specific part of an ecosystem is calculated at a given time. The effects can be aimed at any component of the ecosystem desired such as soil chemistry, or the health and survival of certain tree species or fish (Dupont et al. 2005; Posch et al. 1993). The critical load value is usually determined using a combination of geochemical/soils models and toxicological models or chemical thresholds. Current deposition loads greater than the determined critical load is considered an “exceedance” (Jeffries and Ouimet 2005). Critical loads can be determined for ecologically significant losses of soil cations, survival or health of fish or plant species, or any other ecosystem component considered sensitive to the pollutant of concern; in the case of acid deposition, these loads are usually calculated for sulfur and nitrogen, and are often considered in a combined manner.

Steady-state critical loads allow an evaluation of ecosystem sensitivity at a given point in time. However, because acidification effects are cumulative, another concept called the “target load” is used to determine deposition amounts that will allow the target species or ecosystem component to not be affected by acid deposition over time. Determination of target loads is more complex than that of steady-state critical loads as they require more information for assessing how cumulative impact affects a receptor. The most common approach to determining target loads is through the use of dynamic models. Dynamic models calculate summed amounts of pollutant deposition and in the case of acidification, an acid mass balance is calculated over time, by estimating pre-pollution conditions (hind casting), calibrating to a known data record such as surface-water chemistry, and then forecasting the future acid deposition trajectory and cumulative loads that will be needed to reach a critical level such as stream ANC >50 μeq/L in surface waters, as for example by Cosby et al. (1985). A critical ANC value would be expected to differ depending on the natural buffering capacity of surface waters in a given region. Accurate modeling efforts require data on pre-acidification conditions, which can be obtained from analyzing historical diatom communities in lake sediments and establishing statistical relationships between various species and lake pH or ANC (Smol et al. 1998; Sullivan et al. 1990).

Use of the term “target load” can be confusing because in addition to the dynamic modeling sense described above, this term is also used to describe a policy- and economics-based load that may be less than or greater than the critical load as determined through modeling (Porter et al. 2005; Fisher et al. 2007). For example, the U.S. National Park Service because of their mandate of strict protection of Class 1 wilderness land might choose a target load that is lower than the critical load to insure an extra margin of protection (Porter et al. 2005). The concept of interim target load is also used in this context to establish an interim goal as part of meeting the eventual target load by a certain date.

Critical and target load values will vary depending on the ecosystem receptor which is being studied. Additionally, there can be wide inherent spatial variation in critical loads even for the same receptor within a small area due to differences in geology and soils (Sullivan et al. 2008). For example, in the case of soil acidification one definition of a critical load is when the amount of acid deposition causes no further decrease in the soil’s ability to neutralize acidity (no decrease in soil base saturation). In aquatic ecosystems on the other hand, a critical load might be the deposition amount below which a population of fish, zooplankton, or insects could not maintain itself. The approaches used for calculating critical loads can therefore be varied and are described in the references cited herein. Moreover, the critical load values for soils and water for a certain area will not necessarily be the same, even though they should in theory be related. Jeffries and Ouimet (2005) discuss how critical loads from different environmental components and the use of different calculation approaches can be merged to provide a reasonable synthetic interpretation of conditions.

When the current rate of acid deposition is higher than the calculated critical load, the difference between the two is called an “exceedance,” which provides an indication of the acid deposition reduction needed to allow for no further damage. Soil critical loads and exceedances for acidification have been calculated for eastern Canada (Jeffries and Ouimet 2005; Fig. 6.7) and the United States (McNulty et al. 2007; Fig. 6.8). These maps were produced using different approaches, but they

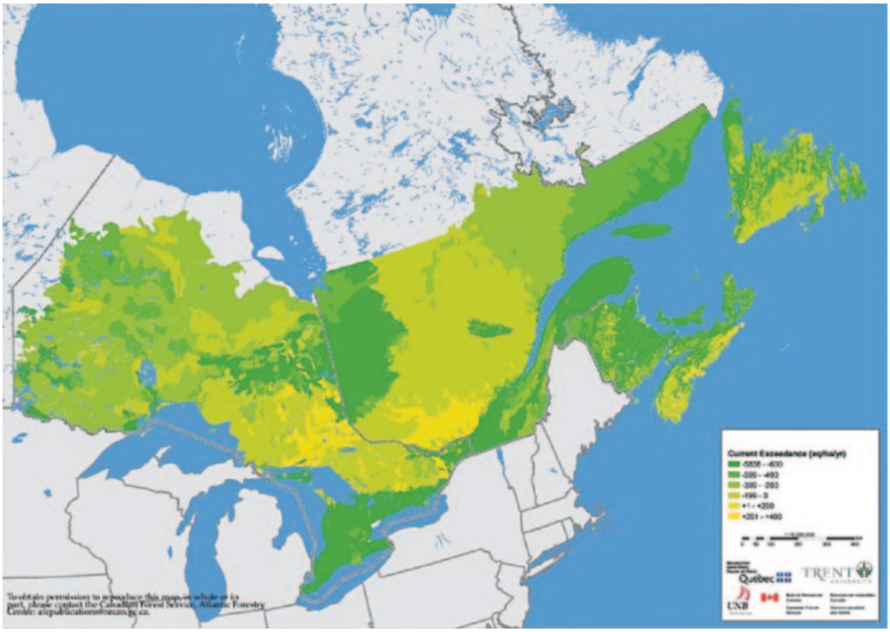


Fig. 6.7 Soil acidification critical load exceedance in eastern Canada. (From Jeffries and Ouimet 2005)

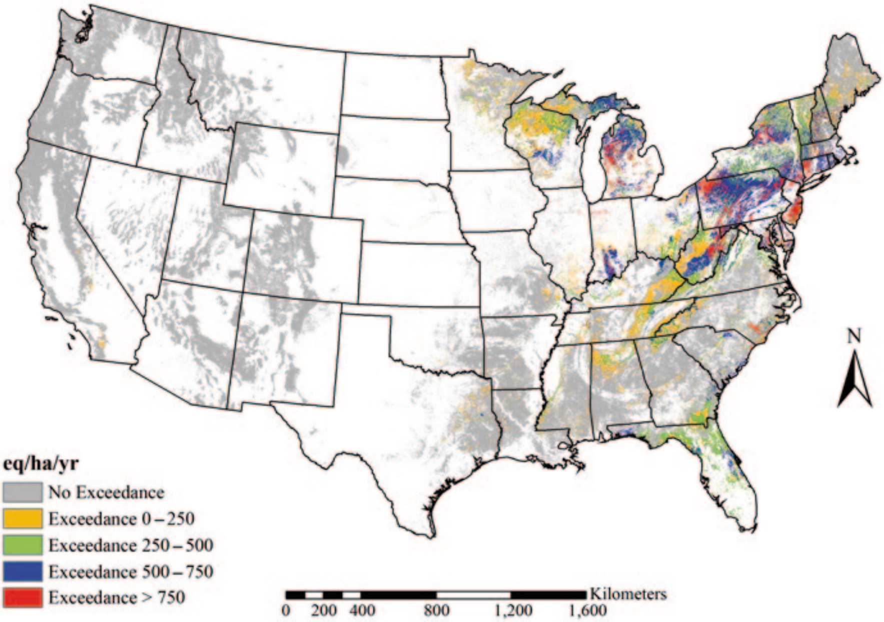


Fig. 6.8 Calculated critical acidification load exceedance in U.S. forest soils. (From McNulty et al. 2007)

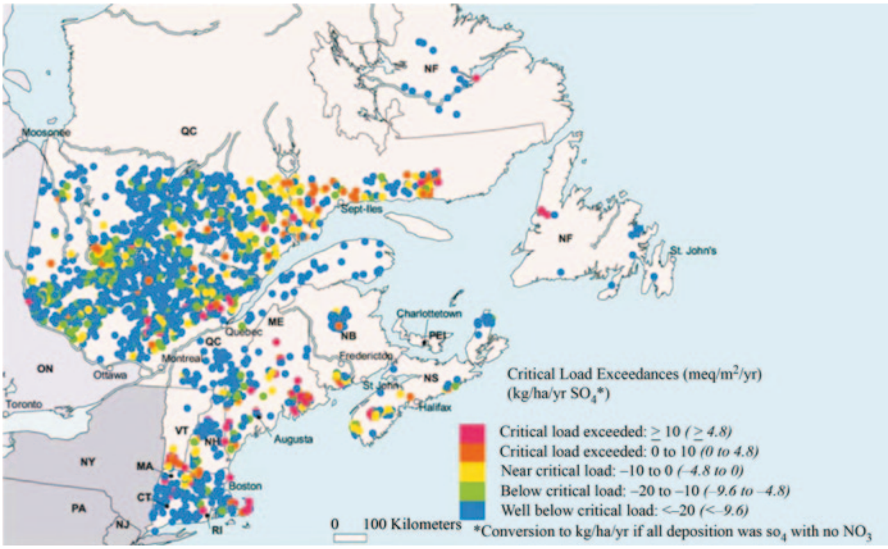


Fig. 6.9 Critical acidifiction load exceedances for lakes in northeastern North America. (Dupont et al. 2005)

all show broad regions of eastern North America that have positive exceedances indicating continued loss of soil base cations, and where forest soils have been most affected by acidification.

In Canada, the Island of Newfoundland and the Province of Nova Scotia, as well as central Ontario and Québec show positive exceedances indicating ongoing loss of soil base cations. In the United States, exceedances are occurring in much of the northeast, the upper Midwest, the Appalachian Mountains of the Mid-Atlantic and southeast, as well as in Florida. These exceedances will result in continued declines in soil base saturation, and are also likely to affect long-term forest health.

Critical load values have also been calculated for individual lakes in northeastern North America in a region stretching from the State of Connecticut to the Island of Newfoundland (Dupont et al. 2005). Using a pH value of 6.0 as a critical limit, a level at which aquatic ecosystems would be protected from acidification effects, critical loads were exceeded in a large number of lakes in the study region (Fig. 6.9). The locations of the lakes where critical loads were exceeded roughly coincide with areas of soil critical load exceedances, but because of different spatial and computational methodologies for lakes and soils, these areas are not necessarily coincident. However, both the lakes and soil maps locate general regions with current acidification problems and where reductions in acid deposition may be needed to prevent continued deterioration.

There have also been many studies of critical nitrogen loads in the Rocky Mountains (Williams and Tonnessen 2000; Sullivan et al. 2005; Baron 2006; Bowman et al. 2006). The work in this region has focused to a greater extent on nitrogen as a nutrient that can alter biological communities. Critical loads calculated for soils, lakes, alpine vegetation, and diatoms in the Front Range of Colorado range from 1.5 kg nitrogen per ha/year to greater than 20 kg nitrogen per ha/year. As an example of a land management agency setting a conservative target load, a value of 1.5 kg nitrogen per ha/year has been set for Rocky Mountain National Park based on demonstrated effects on the aquatic diatom community at levels above this load (Wolfe et al. 2003; http://www.cdphe.state.co.us/ap/rmnp.html#Papers, accessed 4 Jan 2008).

6.2.3.2 Dynamic Modeling of Acid Deposition Effects

Several dynamic models have been developed to predict atmospheric pollutant deposition effects on soils, surface waters, and ground water. In North America, the models most commonly used to predict changes in surface waters and soils are the Model of Acidification of Groundwater in Catchments (MAGIC) (Cosby et al. 1985, 2001) and PnET-BGC (Gbondo-Tugbawa et al. 2001).

MAGIC model outputs were used to predict the potential effects of expected sulfur reductions in eastern Canada on surface water chemistry (Clair et al. 2007). This study showed that anticipated sulfur emissions reductions from Canada and the United States will improve lake water quality in many, but not all parts of the region to levels where aquatic communities would recover to pre-acidification levels. MAGIC was also applied in the most recent National Acid Precipitation Assessment Program report to Congress to demonstrate that additional emissions reductions beyond those to be realized under the 1990 CAAA are needed to provide broad protection to ecosystems in sensitive regions of the United States (NAPAP 2005). Addtional model studies have been done in the eastern United States for the Shenandoah National Park (Sullivan et al. 2008), the Adirondack Region of New York (Chen and Driscoll 2004; Sullivan et al. 2007b), the Catskill region of New York (Chen and Driscoll 2004), the White Mountains of New Hampshire (Gbondo-Tugbawa and Driscoll 2002), and northern Maine (Cosby et al. 1996).

These model results generally show some recovery of water chemistry with past reductions of acid deposition, and additional recovery with implementation of future air quality policies. However, for the most sensitive regions such as the Adirondack Mountains, recovery to pre-acidification levels of lake ANC or soil chemistry does not seem likely in the near future with current air quality policies (Chen and Driscoll 2004; Sullivan et al. 2007b), and the possibility has been raised of a turn around in recovery trends and additional future acidification (Sullivan et al. 2006).

Predictions of surface-water chemistry from the models discussed above have in turn, been linked to statistical models which predict how biological systems may change over time. Sullivan et al. (2004) linked MAGIC outputs to brook trout survival in the Appalachian Mountains of Virginia, and predicted that trout habitat will continue to degrade in the foreseeable future under currently predicted deposition reductions. Clair et al. (2004) linked MAGIC outputs with predicted future changes in deposition to Atlantic salmon habitat in Nova Scotia, and showed that recovery of degraded habitats will not occur for another 60–100 years due to the time needed for watershed soils to recover buffering capacity from the weathering of bedrock.

McNicol (2002) calculated relationships between water chemistry and waterfowl populations in Ontario, and showed that a return to pre-acidification population levels and composition would require additional acid emission cuts than were proposed as of the year 2000.

Generally, dynamic model results indicate a time lag between reductions in acid deposition and ecological recovery in sensitive regions because soil buffering capacity, water chemistry, and biological communities take time to recover, and hinge on factors such as the rate of base cation replenishment due to chemical weathering, net mineralization of soil nitrogen and sulfur, and ecological factors such as population dispersal, competition, and nutrient availability. The model results also show that historical factors such as forest harvesting history and land use history must be taken into account when making future predictions of recovery (Moayeri et al. 2001; Gbondo-Tugbawa and Driscoll 2003; Chen and Driscoll 2004). In general, the acidification modeling results reflect the observational studies of some recovery of surface water chemistry, little evidence of much biological recovery to date, and that there may be a need for additional reductions in deposition before a return to pre-acidification conditions can be expected,after accounting for ecosystem recovery lag-times (see also Chap. 12). The hardest hit and most sensitive regions may never fully recover under any future emission scenarios currently envisioned (Chen and Driscoll 2004).

6.2.3.3 Excessive Reliance on Measured ANC as the Sole Indicator for Acidification Assessment

A potential weakness in many critical load, modeling, and trend studies regarding recovery from acidification is an over-reliance on ANC as an indicator of recovery. In most monitoring networks in North America, measured ANC values based on a Gran titration are the principal indicator of acid-base chemistry. Measured ANC reflects in part contributions from organic acids and other constituents, so basing recovery assessments and model evaluations of future acid-base conditions solely on measured ANC can be misleading. A recent study advocates using the base cation surplus (sum of base cations minus acid anion concentrations after accounting for strong organic acidity) to better evaluate acid-base conditions in surface waters (Lawrence et al. 2007); indeed, the base cation surplus is similar to measures of "calculated" or "charge balance" ANC that have been used in some assessments (Driscoll and Newton 1985; Hemond 1990).

A second reason for not relying solely on ANC is that evidence suggests hysteresis exists in the recovery of base cation concentrations in many surface waters. This means that calcium and magnesium concentrations were higher at a given ANC value at the time that waters were being acidified, and are now at lower values at the same ANC value during recovery (Likens et al. 1996). This hysteresis behavior is likely due to long-term base cation depletion from soils. The implications of base cation depletion for aquatic and terrestrial ecosystems includes potential nutrient limitation effects on the survival and reproductive success of organisms such as song birds, sugar maple, and the zooplankton Daphnia (Hames et al. 2002; Houle et al. 2002; Yan et al. 2003; Hallett et al. 2006). While there is some awareness of this “downside” of recovery within the scientific community, there still exists an over-reliance on just the ANC values of surface waters to evaluate it. This observation suggests a need for scientific studies that more fully evaluate recovery of soil chemistry as well as a full suite of surface-water chemistry parameters, and a need for more rigorous consideration of base cation depletion effects in assessments of the ecosystem effects of clean air policies.

6.2.3.4 Modeling of Excess Nitrogen from Atmospheric Deposition in Large Rivers

The discussion in the previous section was focused mainly on monitoring and modeling of acidification, and in this context most of the existing surface-water chemistry models consider the nitrogen cycle in varying levels of complexity from the relatively simple approach used in MAGIC (Cosby et al. 1985) to consideration of more processes in greater detail such as in PnET-BGC (Gbondo-Tugbawa et al. 2001). But in addition to its effects on acidification, atmospheric nitrogen deposition is also of concern because nitrogen availability may limit biological growth in some settings and may alter species diversity in many biological communities such as in alpine ecosystems (Wolfe et al. 2003; Bowman et al. 2006), and especially in estuarine ecosystems (Diaz 2001). Large estuarine watersheds in the United States where nitrogen-driven eutrophication has been reported typically have large human populations and many sources of nitrogen, among which atmospheric deposition can vary from minor to dominant (Boyer et al. 2002).

Many modeling approaches have been developed to accurately predict the role of atmospheric nitrogen in the export of nitrogen in multi-source watersheds (Alexander et al. 2002), of which the Spatially Referenced Regressions of Contaminant Transport on Watershed Attributes (SPARROW) is among the most widely applied (Smith et al. 1997). SPARROW is based on non-linear regression of spatially-explicit relations between various land uses and sources of nitrogen combined with a simple empirical model that accounts for in-stream losses during transport in the river network. The model has been applied primarily in large river/estuarine basins such as the Mississippi and Chesapeake Bay (Alexander et al. 2000, 2001). Other models exist to predict nitrogen export in surface waters, and these range from simple export coefficient models, to sophisticated multi-media process-based deterministic models such as the Cheapeake Bay watershed model (Linker et al. 2000) or the Integrated Biosphere Simulator (Donner et al. 2002).

These models seem to work best at the large watershed scale and produce relatively poorer predictions of nitrate export with decreasing drainage area, probably due to an inability to accurately represent storage and gaseous losses at small scale (Caraco et al. 2003). Even conceptual nitrogen cycling models such as the nitrogen saturation model seem unable to accurately predict trends and patterns in stream nitrate export in many regions in forested watersheds whose only source is atmospheric deposition (Goodale et al. 2003). These results suggest that either the nitrogen cycle is inadequately understood and represented in these models, or that complex interactions among factors that affect nitrogen cycling processes are not adequately considered (Goodale et al. 2005).

6.2.3.5 Predicting Atmospheric Mercury Effects in the Environment

Measurement techniques that include wet deposition collectors, throughfall, litterfall, and gas-analyzing instruments have been developed in attempts to measure the total deposition of mercury onto landscapes. Many of these studies, especially those that sample gas and particles directly must rely on an inferential model to obtain deposition velocities of mercury species (Lindberg et al. 1992; Meyers et al. 1998). Other modeling approaches have been developed that estimate mercury deposition at regional, continental, and global scales (Bullock and Brehme 2002; Seigneur et al. 2004; Miller et al. 2005), using statistical relationships and first principle assumptions to simulate the effects of atmospheric mixing processes, chemical reactions, deposition velocities, and landscape complexity on mercury deposition.

While atmospheric deposition of mercury is the principal source to most ecosystems that have high concentrations of methyl mercury in predator fish, many studies have demonstrated that the presence of high levels of mercury in surface waters and biota is not necessarily dependent on an immediate source of atmospheric mercury deposition, but is governed by the ability of ecosystems to convert mercury to the methyl form, especially in the presence of sulfate, and to transport that methyl mercury to surface waters where it can be taken up by aquatic biota. In particular, geographical modeling studies have shown that the presence of wetlands is a principal factor responsible for elevated levels of mercury in water (Dennis et al. 2005), fish (Kamman et al. 2005) and fish-eating birds (Driscoll et al. 2007b).

Mercury modeling is at an earlier stage of development than that of acidification models because there is a shorter history of high-quality data available, and there remains a great deal of uncertainty in the complex processes that affect the mercury cycle from the atmosphere through terrestrial ecosystems and to aquatic ecosystems, including strong interactions with acidification (Kamman et al. 2005; Driscoll et al. 2007a). Improved mercury models will be necessary to provide more tightly constrained estimates of the timing and magnitude of responses of ecosystems to future changes in air emissions of mercury. Improvement in mercury models are currently hindered by high uncertainties in the residence time of deposited mercury, the rates of numerous fluxes and processes within ecosystems, and the size and responsiveness of various mercury pools in ecosystems. Nonetheless, several mercury cycling models have been developed in recent years (Chen et al. 2004; Brown et al. 2007; Knightes and Ambrose 2007).

One of the principal models applied to lakes in North America is the process-based deterministic Mercury Cycling Model (MCM) (Hudson et al. 1994). This model has been applied in the Adirondack region of New York State (Driscoll et al. 1995), in Wisconsin (Hudson et al. 1994), and in the Florida Everglades (Atkeson et al. 2003). Given the rapid development of scientific understanding of the mercury cycle in the past several years, and prospects for increased understanding through application of isotope tracers of the mercury cycle and other methods, it seems likely that better mercury models will become available in the near future as our understanding and ability to quantify rates of mercury transformations in ecosystems further improves.

The critical loads concept discussed above for sulfur and nitrogen deposition, also has been applied to mercury and other trace metals. In Europe, studies and mapping of critical loads of metals date to the 1990s (DeVries et al. 1998). A difference between critical loads relative to acidification and those of metals is that metal critical loads are often set at a value relative to harmful effects on human health rather than on ecosystem structure and function as with sulfur and nitrogen (Lofts et al. 2007). This approach is still highly controversial because current data and models cannot yet tell us with certainty a “safe” level of atmospheric mercury deposition. Therefore, a critical loads approach to mercury depositon has not yet been applied in North America. Nevertheless, the approach is useful conceptually and is generating a great deal of research designed to produce the necessary supporting information. It seems likely that critical loads approaches for mercury and other metal will become more developed in North America as scientific knowledge of trace metals effects on human and ecosystem health advances further.

6.2.3.6 Predicting Future Ozone Effects

The interaction of ozone with trees is a complex process that varies in response to a host of environmental, ecological, and other factors (Kubiske et al. 2006; Percy et al. 2002) and this complexity presents great challenges for scaling impacts beyond the tree level (Samuelson and Kelly 2001). Many models used previously to predict forest productivity change due to ozone effects (Ollinger et al. 2002; Felzer et al. 2004) have assumed a degree of linearity in response to ozone exposure. Yet, we know that plant response to ozone is intrinsically non-linear. Increasing CO_2 and ozone levels can lead to both stomatal closure, which reduces the uptake of either gas, and in turn limits the damaging effect of ozone and the CO_2 fertilization of photosynthesis.

Recently, Sitch et al. (2007) have estimated the impact of projected changes in ozone on the land-carbon sink, using a global land carbon cycle model modified to include the effect of ozone deposition on photosynthesis and to account for interactions between ozone and CO_2 through stomatal closure. For a range of sensitivity parameters based on manipulative field experiments, they found a significant suppression of the global land-carbon sink as increases in ozone affected plant productivity. As a consequence, CO_2 accumulation in the atmosphere was enhanced. They suggest that the resulting indirect radiative forcing by ozone effects on plants could contribute to global warming to a greater extent than the direct radiative forcing due to tropospheric ozone increases.

The United States and Canada currently use exposure-based metrics to assess the effect of ozone on vegetation. In North America, the best available scientific knowledge, balanced by social, economic, and political considerations, is employed to set ambient air quality standards for regulatory purposes. The United States and Canada recently established the ozone air quality standard metric form as “the 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentration” (Federal Register 1997; CCME 2000). In the United States, there is a primary standard (human health-based) and a secondary standard (welfare-based) that can be different or the same (Percy et al. 2003). The current EPA primary National Ambient Air Quality Standard (NAAQS) for ozone is set at 75 ppb. At this time, the secondary standard is the same as the legally-binding primary standard. In Canada, the metric form is the same as in the United States, but the level differs. The Canada Wide Standard (CWS) for Particulate Matter and Ozone (CCME 2000) established a human health-based target value of 65 ppb ozone.

Musselman et al. (2006) concluded that until effective dose models are developed, “…exposure-based metrics appear to be the only practical measure for use in relating ambient air quality standards (in North America) to vegetation response.” Also, exposure–response models using ozone-exposure indices developed around ambient-air quality standards have the potential to improve risk assessment, strengthen accountability, and at the same time, enhance scientific literacy, leading to increased support for science (Percy and Karnosky 2007).

Using five-years of co-measured ozone, meteorology, and growth response, Percy et al. (2007) have developed exposure-based regression models that predict *Populus tremuloides* (trembling aspen) growth change within the North American ambient air quality management context. The models included growing season fourth-highest daily maximum 8-hour average ozone concentration (NAAQS and CWS metric form), growing degree days and wind speed. The models had high statistical significance, high goodness of fit, include 95% confidence intervals for tree growth change, and are simple to use. Averaged across a wide range of clonal sensitivity, during 2001–2003 growth change over most of the 26 Mha area where *P. tremuloides* are distributed was estimated to range from 0% (no impact) to strong negative impacts (−31%).

However, Calabrese (2005) has convincingly stated the case that at low concentrations, stimulation of biological response can also occur (a hormetic relationship). In the science of ozone forest response, investigators have too often placed emphasis on finding only strongly negative responses (Manning 2005) but Calabrese (2005) has convincingly stated the case for the hormetic dose–response relationship as underlying the toxicological basis for risk assessment.

When considering relevance of this current research within the ambient exposure-based metric context (Foley et al. 2003), it is important to note that the growing season 4th highest daily maximum 8-hour average ozone concentration indicator used in models represents the biologically relevant portion of the NAAQS (Federal Register 1997) and CWS (CCME 2000).

Regression analyses by Percy et al. (2007) have further demonstrated that annual growing season 4th highest daily maximum 8-hour average ozone concentration performed much better as a single ozone exposure index for trembling aspen and white birch cross-sectional area growth than did W126, SUM06, AOT40 averaging for ozone concentrations (defined in http://www.asl-associates.com/flag.htm), and maximum 1-hour average ozone concentration. Growing season 4th highest daily maximum 8-hour average ozone concentration was most closely associated with the actual measured response in the biological endpoint. The W126 index was found to significantly overestimate the negative growth response of aspen and birch to ozone. The above discussion shows that the choice of technical standards, criteria and models used in assessing and predicting ozone effects are critical and need to be further carefully assessed.

6.3 Multipollutant Effects on Ecosystems

Individual atmospheric stressors and their effects were discussed separately in the above sections in order to describe the major stresses and changes these pollutants cause in soils, water chemistry, and plant and animal communities. However, atmospheric stressors rarely operate individually. Ecosystems are usually simultaneously affected by two or more atmospheric pollutants or other stressors, whose effects can combine to either amplify or alleviate the effects on receptor ecosystems. In this section, we describe some of the best understood interactions between atmospheric pollutants to show that ecosystem recovery and change must consider more than just a single pollutant approach to ameliorate ecosystem effects.

By the late 1980s, researchers studying acid deposition effects were focusing on the combined effects of sulfur and nitrogen deposition. Recent research has increased our understanding of multipollutant interactions such as those of nitrogen and sulfur with calcium, as well as mercury with sulfur deposition and soil and surface water acidification. Below, we highlight some of this recent work. Additionally, given recent climate change research and the high likelihood of larger variations in temperature and precipitation in coming decades, it is imperative to understand how climate and the carbon cycle interact with nitrogen, sulfur, ozone, and mercury. Greater understanding of these multipollutant interactions will better provide: (1) science-based adaptive strategies to maintain ecosystem health and productivity for land owners and managers, and (2) justification and accountability for control of multiple emissions sources.

6.3.1 Nitrogen, Sulfur, and Mercury Pollutant Interactions in Ecosystems

Acid rain is fundamentally a multipollutant problem with sulfuric and nitric acids as well as ammonium all contributing to ecosystem acidification. Although early acidification research focused more strongly on sulfuric acid, the importance of nitric acid has generally been well recognized since the 1980s, and most investigations of acid deposition and acidification since that time have studied both sulfuric and nitric acid effects. In the United States, this multipollutant work has resulted in legislation such as Title IV of the 1990 CAAA, and the proposed Clean Air Interstate Rule of 2005 (CAIR) that address both sulfur and nitrogen oxide pollutants.

Research on mercury cycling and bioaccumulation in the environment has identified important links between atmospheric sulfur deposition, acidification, and bioaccumulation of mercury in fish. Conversion of mercury to the toxic methyl form that can be readily bioaccumulated by fish and other biota is strongly associated with sulfate-reducing bacteria, although other microorganisms such as iron-reducers as well as abiotic methylation are known to occur as well (Ullrich et al. 2001). Several studies have demonstrated that additions of sulfate increase the methylation rate and concentrations of methyl mercury in waters and thus biota (Gilmour et al. 1992; Branfireun et al. 1999; Jeremiason et al. 2006). The mechanism is believed to involve the formation of neutral sulphide complexes that are passively taken up by methylating bacteria (Drott et al. 2007). Researchers have noted in some environments such as the Florida Everglades and in salt marshes, the rate of sulfate-reduction in sediments is inversely related to the rate of mercury methylation suggesting a threshold above which sulfur changes from stimulating to inhibiting methylation (Choi and Bartha 1994; Gilmour et al. 1998). It appears that in highly reducing conditions where sulfide concentrations can be quite high, charged mercury sulfide complexes inhibit the uptake of mercury into sulfate-reducing bacteria (Gilmour et al. 1998). Despite this caveat for sulfidic environments, it is likely that in many surface waters with little supply of sulfate from natural mineral sources, changes in anthropogenically-derived sulfate may be an important control on methyl mercury concentrations in water and fish (Hrabik and Watras 2002). In the absence of decreasing trends in atmospheric mercury deposition, decreases in atmospheric sulfur deposition alone may reduce mercury concentrations in freshwater fish (Drevnick et al. 2007). Although it is well recognized that some mercury emission reductions have been realized through laws aimed at sulfur and nitrogen emissions, EPA has historically treated sulfur and mercury emissions in separate rules such as in the recently court-vacated CAIR and the Clean Air Mercutry Rule (CAMR). However, the close link observed between sulfate reduction and mercury methylation in some settings suggests that sulfur emissions reductions could be used in conjunction with mercury emissions reductions to address mercury health effects and bioaccumulation.

Another link between acid deposition and mercury deposition is through the commonly observed inverse relationship between pH and mercury in waters and fish (Kamman et al. 2004; Wiener et al. 2006). Low pH conditions in surface waters, which are often driven by acidification from atmospheric sulfur and nitrogen deposition, seem to generally favor higher mercury concentrations in biota in the absence of other strong drivers. Several hypotheses have been offered to explain pH effects on methylation rates and bacterial uptake of mercury (Kelly et al. 2003), but no single mechanism is agreed as responsible for the observed pH effect (Munthe et al. 2007). Addtionally, since pH and sulfate concentrations are often correlated in waters acidified by atmospheric deposition, both acidity and the presence of sulfate for reduction may jointly act to control methylation and uptake in many systems.

Nitrogen and phosphorus availability are also known to potentially affect mercury concentrations in fish and other aquatic biota, but in an opposite manner to that of sulfate. An inverse relationship between aquatic productivity and methyl mercury concentrations in fish has long been recognized in a variety of fresh waters—the so called "biodilution" hypothesis (Norstrom et al. 1976). In the majority of North American fresh waters, phosphorus is the nutrient that limits aquatic productivity, and increases in phosphorus have been shown to widely affect mercury biodilution (Wiener et al. 1990; Meili 1991; Kamman et al. 2004; Driscoll et al. 2007a). The contribution of nitrogen to increased biological productivity is not as common or widespread as that of phosphorus excepting some fresh waters and in estuarine environments (Lange et al. 1993). Moreover, biodilution is not evident at all sites, probably due to the complexity of other factors such as pH, presence of wetlands, climate, and food web structure that can affect mercury bioaccumulation (Stafford and Haines 2001).

Nitrate is also known to inhibit sulfate reduction through competition for substrate (electron donors) in many environmental settings (Westermann and Ahring 1987). Since mercury methylation is strongly related to sulfate reduction in many ecosystems, nitrate may act to inhibit methylation although this nitrate-inhibition effect has not yet been studied in relation to mercury bioaccumulation.

6.3.2 Climate Change and the Carbon Cycle

North America has warmed by about 0.6°C during the twentieth century, and this warming has accelerated since the 1970s (Jones and Moberg 2003). The scientific consensus is that recent climate warming is believed to be caused by increases in greenhouse gas concentrations that largely result from human activities such as the burning of fossil fuels and deforestation (IPCC 2007). The warming measured to date is believed to be driven mainly by CO_2 concentrations that have increased from about 280 ppm in 1750 to 381 ppm in 2006 (Canadell et al. 2007), and are at their highest levels in the past 650,000 years (Siegenthaler et al. 2005). Increasing concentrations of other greenhouse gases such as methane, nitrous oxide, and chlorofluorocarbons have also been measured in recent decades, and together these gases are believed to account for about 37% of current radiative forcing (Forster et al. 2007).

Information from studies of projected future energy consumption and economic growth combined with global climate models indicate that increases in greenhouse gas concentrations accompanied by additional warming are likely to continue for the foreseeable future (see also Chap. 11). However, increased awareness of the consequences of global warming may impel actions to reduce greenhouse gas emissions and slow the current warming trend in coming decades. Nonetheless, these ongoing changes in atmospheric CO_2 concentrations and air temperature have already had effects on the manner in which ecosystems interact with nitrogen, sulfur, and mercury air pollutants. Additionally, ecosystem modeling has projected future changes in air pollutant—climate interactions that have potentially large consequences for air pollutant impacts on North American ecosystems (see also Chap. 11).

In this section, we highlight a few of the better known and widely studied implications of changes in climate and the carbon cycle on the interactions of sulfur, nitrogen, mercury, and ozone in these ecosystems. Interpreting how increased CO_2 concentrations and climate warming may impact air pollutant effects on North American ecosystems is difficult because of confounding interactions among an array of factors that are likely to change over the same temporal scales including solar radiation, particulates in the upper troposphere, and the global water cycle. For example, increased CO_2 concentrations may decrease photosynthesis rates in some plant species, but simultaneous warming will likely change climate adaptation of other species, which will likely affect competitive plant interactions while at the same time water availability may be changing. The result of these ongoing and likely future multiple and simultaneous changes is a set of complex possible consequences in how ecosystems interact with air pollutants that does not lend itself to simple interpretations.

6.3.2.1 Interactions of the Carbon Cycle with Sulfur and Nitrogen Pollutants

Simultaneous increases in atmospheric CO_2 concentrations and air temperature may affect North American ecosystems in a complex manner that includes changes in growth rates of vegetation, adaptation of aquatic and terrestrial species to their environments, the rates of microbial processes, and the storage of carbon and nitrogen in landscapes (Iverson and Prasad 1998; Mohseni et al. 2003; Magnani et al. 2007). The rates of nearly every biogeochemical process that affects the cycling of atmospherically-deposited sulfuric and nitric acids through ecosystems such as chemical weathering, nitrification, sulfur and nitrogen mineralization, and many others is likely to be affected by changes in climate. For example, laboratory studies show that the rates of chemical weathering and nitrification will increase with increasing temperature if all other factors are held constant (White et al. 1999; Dalias et al. 2002). However, future climate warming in North America is likely to be accompanied by complex changes in the hydrologic cycle that might include increases in precipitation in some regions, and decreases in others in addition to increased rates of evapotranspiration that may be tempered by less stomatal opening in response to increased CO_2 concentrations (Milly et al. 2005; Gedney et al. 2006). Therefore, applying simple equations that describe the effects of temperature on the rates of biogeochemical processes will likely not provide adequate predictions in a changing climate.

One interaction between climate change and atmospherically-deposited sulfur pollutants was identified in the 1990s when the boreal region of Canada experienced severe droughts. When streams and lakes in this region eventually experienced high streamflow conditions following the droughts, large pulses of sulfuric acid were exported from terrestrial catchments (Bayley 1992; LaZerte 1993).

These acid pulses were believed to originate from the oxidation of reduced sulfur compounds in wetland soils and lake sediments that were previously deposited and stored during earlier wetter and cooler climatic conditions. This drought-induced reacidification has demonstrated ecological effects on Canadian boreal waters (Yan et al. 1996), and can delay recovery from decreased atmospheric sulfur deposition.

A large number of studies have explored how climate change may affect linkages between the nitrogen and carbon cycles. There is evidence to support the idea that warmer temperatures increase the rate of nitrification and nitrate leaching in humid ecosystems of the Northeast that receive high loads of atmospheric nitrogen deposition (Murdoch et al. 1998). However, the likely long-term persistence of these patterns with future climate change and increases in atmospheric CO_2 concentrations is unknown. One example of a confounding factor is that climate warming is expected to result in a northward migration of sugar maple from New York and New England to higher latitudes in Canada, to be replaced by oak-hickory forest that is currently dominant in the mid-Atlantic region (Iverson and Prasad 1998). Because soils under sugar maple have high rates of nitrification and those under red oak tend to have low nitrification rates, loss of sugar maple and invasion by red oak may diminish the effects of nitric acid-driven acidification and result in lower nitrogen loads in streams draining forested regions (Lovett and Mitchell 2004). This is only one example of numerous likely and possible changes in ecosystem storage and processing rates of nitrogen and sulfur air pollutants as a result of CO_2-driven climate change in coming decades. This discussion points to the need for air pollutant ecosystem effects models that consider climate change in future projections. Currently, our knowledge of these climate change outcomes is not certain enough to be incorporated into quantitative predictions; however, adequate knowledge currently exists to at least justify “range of uncertainty” model predictions.

An important concern regarding nitrogen air pollutant effects and climate change is how increases in atmospheric CO_2 concentrations will interact with nitrogen limitation of production in forested ecosystems of North America. Despite the acknowledged role of air pollutant NO_x over much of North America, most temperate and boreal forested ecosystems have shown evidence of responding to increasing nitrogen deposition through increased net ecosystem productivity and carbon sequestration (Magnani et al. 2007). Areas that receive high levels of atmospheric nitrogen deposition (>10 kg nitrogen per ha/year) and show signs of nitrogen saturation may take up lesser amounts of carbon because these ecosystems are no longer nitrogen limited and may be experiencing soil acidification, nutrient imbalances, and poor tree health (Aber et al. 1998). However, recent evidence also suggests that such areas are limited in geographic extent in North America (Magnani et al. 2007). In thinking about the role of future changes in climate and CO_2 concentrations on forested ecosystems, we again caution against forming simple conclusions or in using past evidence alone to guide conclusions; other factors such as changes in water availability, trace element availability, and disturbance regimes will likely confound a simple outcome (Dale et al. 2001; Hungate et al. 2004).

Given the complex array of changes that are possible in a changing climate, we conclude that studies and data from well-monitored intact ecosystems are critical to our evolving understanding of how air pollutant effects such as acidification and nitrogen leaching may be altered in a changing climate. It is also important to consider that climate warming and increased CO_2 concentrations are but two changes occurring in the landscape. Past and ongoing changes in land use and land management have dramatically affected North American ecosystems, and understanding the consequences of these changes in land use as well as those of natural disturbances will continue to be important for understanding the effects of future climate change on ecosystem interactions with sulfur and nitrogen air pollutants (Pielke 2005).

6.3.2.2 Interactions of the Carbon Cycle with Mercury

Mercury has a complex cycle in the environment that includes natural and human emissions sources, wet and dry deposition, biological and abiological storage and cycling processes, and bioaccumulation. Many of these transfer and storage processes may be altered by changes in air temperature and precipitation. For example, net methylation is the key process that facilitates uptake, bioaccumulation, and toxicity of mercury in aquatic ecosystems, and like most microbiological processes, methylation rates tend to increase with increasing temperature (Wright and Hamilton 1982). However, many other factors such as pH, sulfate availability, redox status, and carbon availability also affect methylation, making it difficult to predict methyl mercury changes by extrapolations based solely on likely temperature responses.

The emissions that originate from soils, fresh waters, and the oceans may increase as air temperatures increase, though the overall effect of climate change is to introduce greater uncertainty in models of mercury transport and deposition (Lindberg et al. 2007). One outcome of climate warming that seems likely to persist in the twenty-first century is increased mercury emissions from northern peatland soils associated with warming, drying, and increased wildfire frequency (Turetsky et al. 2006). Northern peatlands hold large mercury stores, and wildfire emissions seem likely to exacerbate mercury release in coming decades in boreal ecosystems of western Canada. Though the changes identified here are likely in the future, the current state of knowledge does not yet allow accurate quantification of the extent of these changes. As more information becomes available, this problem should be corrected, and allow the development better predictive mercury—climate change models.

6.3.2.3 Increasing Dissolved Organic Carbon Concentrations: A Case Study of the Interaction of Multipollutant Ecosystem Effects and Climate Change

In most freshwaters, dissolved organic carbon (DOC) is generated from the dissolution of soil organic matter and leaching into drainage streams or lakes, though in very large lakes the principal source is algal and bacterial cells (Thurman 1985).

DOC is a major contributor to the color and transparency of surface waters and increasing DOC concentrations generally reduce light penetration and the thickness of the photic zone where primary productivity occurs. DOC affects thermal stratification and water temperature as well, all of which have implications for aquatic ecosystem dynamics (Snucins and Gunn 2000).

Additionally, much of the DOC present in waters is in the form of natural organic acids, so that increasing DOC affects water pH values, while at the same time DOC concentrations are dependent on and respond to changes in pH. DOC also binds metals in aquatic systems, and increasing DOC concentrations would be expected to increase the aquatic transport of a variety of metals that include aluminum and mercury. In the case of aluminum, metal—organic transport would be expected to reduce the bioavailability and toxicity of the metal, but in the case of mercury, increased metal—organic complexation might increase bioaccumulation. Finally, naturally occurring DOC plays an important role in the formation of carcinogenic disinfection by-products during chlorination (Chow et al. 2003) and can contribute to deterioration of water quality by promoting the growth of heterotrophic bacteria in water distribution systems (Escobar et al. 2001).

Widespread increases in DOC concentrations in North American and European surface waters have been documented during the past decade (Driscoll et al. 2003; Evans et al. 2006; Monteith et al. 2007), though some waters in eastern Canada and the southeastern United States show either no trend or significant decreasing DOC trends (Keller et al. 2003; Monteith et al. 2007; Clair et al. 2008). These widespread variations in DOC concentrations are of geochemical and ecological consequence and provide an excellent case study of the interaction of multiple air pollutants with climate change and the carbon cycle, and indicate how unforeseen ecological consequences can emerge. Identification of DOC trends and their ecological consequences also illustrates the value of data from long term monitoring networks for identifying problems or issues for which these networks were not necessarily originally designed. Climate change and mercury-related trends are also being tracked by some monitoring networks originally designed to track acid precipitation and highlight the importance of good planning and monitoring protocols.

Six causes have been put forth to explain why DOC concentrations are changing in remote freshwaters that are not greatly influenced by human land use: (1) decreasing atmospheric sulfur deposition (Evans et al. 2006; Monteith et al. 2007), (2) decreases in sea salt deposition (Monteith et al. 2007), (3) chronic inputs of atmospheric nitrogen deposition (Findlay 2005), (4) climate warming (Worrall et al. 2003; Clair et al. 2008), (5) changes in precipitation amount (Hudson et al. 2003; Worrall et al. 2003), and (6) changes in incident solar radiation (Hudson et al. 2003). Reduced levels of sulfur deposition are thought to likely play an important role in increased DOC concentrations in many surface waters in North America (Monteith et al. 2007). Decreases in sulfur deposition over the past 10–20 years have resulted in increasing pH and decreasing ionic strength in many waters, both of which should increase the solubility of organic matter in soils and sediment, and even DOC trends that appear to be driven by drought occurrence may actually result from drought favoring the oxidation of previously reduced sulfur compounds (Clark et al. 2006).

Although the possible role of nitrogen deposition in increasing DOC trends has been raised (Findlay 2005), tests of the mechanism invoked as the cause of DOC increases—suppression of lignin degrading enzymes—have been inconclusive to date (DeForest et al. 2005; Waldrop and Zak 2006). In contrast, soil carbon/nitrogen ratios are positively correlated with surface water DOC export across a wide geographic range and drainage basin sales in Europe and North America (Aitkenhead and McDowell 2000; Aitkenhead-Peterson et al. 2005). Since atmospheric nitrogen deposition is inversely correlated with soil carbon/nitrogen (Aber et al. 2003), the implication is that an inverse relation between atmospheric nitrogen deposition and surface water DOC concentrations might be expected if the carbon/nitrogen spatial model described above is also valid for explaining temporal changes. Together, these studies indicate an uncertain role for atmospheric nitrogen deposition, and that nitrogen deposition is not a significant explanatory factor for DOC trends across a range of surface waters in Europe and eastern North America (Monteith et al. 2007).

Climate variation is also a factor likely to at least partly explain surface water DOC trends in some regions (Hudson et al. 2003; Worrall et al. 2003). Fundamentally, warmer soil and sediment temperatures should increase the decomposition rates of organic matter; however, variations in moisture, nutrient availability, redox conditions, and other variables would be expected to mask a simple DOC—temperature relationship (Giardina and Ryan 2000). Research in Canadian lakes has highlighted the important roles of drought-wetting cycles as well as solar radiation on surface water DOC concentrations (Dillon and Molot 1997; Schindler 1998; Hudson et al. 2003). In contrast to other regions, in many parts of Canada either no trend or decreasing trends in DOC concentrations have been observed, although the most recent evidence suggests that DOC is increasing at many monitored lakes in Ontario and Quebec (Monteith et al. 2007). Since Arctic regions of North America have experienced some of the greatest warming trends on Earth, climate warming is expected to significantly increase DOC concentrations and fluxes in surface waters (Clair and Ehrman 1998; Frey and Smith 2005); however, data from the Yukon basin supports decreased DOC export, which may result from increased mineralization in the active soil permafrost layer (Striegl et al. 2005).

Regardless of the factors driving increasing DOC trends in surface waters, these trends have potentially serious ecological and water management consequences. Fundamentally, changes in DOC concentrations in aquatic ecosystems will reflect the intersection of a wide range of air pollutants and climate change factors, and future changes in DOC export are expected to alter aquatic food webs, affect mercury transport and bioaccumulation, affect the recovery of acidified ecosystems, possibly accelerate the delivery of carbon to the earth's oceans, and pose challenges for water suppliers.

6.3.2.4 Ozone Effects on Forests with Climate Change

It is widely perceived that future climate change will lead to increased growth and range distribution of some forests (Cox et al. 2000). This warming is largely being driven by increased radiative forcing caused by rising levels of greenhouse gases. The third most important greenhouse gas contributing to global average radiative forcing is tropospheric ozone (Rawaswamy et al. 2001). In the lower troposphere, surface level ozone has become one of the most pervasive air pollutants at the terrestrial biosphere–troposphere interface (Fowler et al. 1999).

Using a long-term, ecosystem level free-air exposure system at the Aspen FACE (Free Air Carbon Dioxide Enrichment) Experiment, Karnosky et al. (2003) demonstrated that elevated ozone at relatively low concentrations can significantly reduce the growth enhancement of elevated CO_2. The suites of responses to elevated CO_2 and/or ozone at the Aspen FACE project have been remarkably consistent across functional groups, species, and trophic levels. These results followed similar trends to those of many agricultural crops, other hardwood trees and a few conifers. Taken together, these studies on plants of different genetic backgrounds, growth characteristics, and life histories suggest that ozone can seriously alter the capacity of vegetation to grow under elevated CO_2 and to sequester carbon. Karnosky et al. (2003) further stated that an understanding of ozone as a moderator of CO_2 responses is essential to improve global models of terrestrial net primary production which currently predict that ozone levels in the United States can largely offset increased forest productivity caused by increasing atmospheric CO_2 concentrations.

While elevated levels (circa. 550 ppm) of atmospheric CO_2 have generally moderated the detrimental responses of ozone, some noticeable exceptions include the long-term growth suppression of sugar maple and paper birch, which could not have been predicted by studies of these two important greenhouse gases applied singly or for a short-term (Karnosky et al. 2005). Elevated levels of CO_2 alone caused 20% growth increases in *Betula papyrifera* (White birch) and 30% increases in *Populus tremuloides*. For *P. tremuloides*, this amounted to an increase of over 1 million km^2, similar in size but opposite in direction to the effect of ozone. Simultaneous exposure to ozone and CO_2 had offsetting effects in *B. papyrifera* and *P. tremuloides*. Inexplicably, the competitive advantage *B. papyrifera* was simulated to have under ozone exposure disappeared when CO_2 was also present, so that there are complex interactions occurring which are still not understood.

Another result from the landscape level that was not predictable from the physiological effects, was that the presence of CO_2 exacerbated the negative effect of ozone on *Acer saccharum* (Sugar maple) abundance, causing it to decrease by over 30% (Karnosky et al. 2005). These longer-term data highlight the importance of bottom-up changes caused by the combined effects of CO_2 and ozone on food quality and the long-term population dynamics of forest pests. Further, they suggest links between net primary productivity (NPP—the buildup of plant matter through photosynthesis), the biochemical constituents of plant litter, and the metabolic responses of microbial communities which are crucial to a mechanistic understanding of how these greenhouse gases will alter soil carbon and nitrogen cycling, as well as long-term forest ecosystem productivity (Karnosky et al. 2005).

In terms of soil, root studies at Aspen FACE suggest that elevated CO_2 increases the flux of carbon from root systems to the soil, while elevated ozone alters whole plant source–sink relationships, resulting in more rapid root turnover and a smaller crop of standing fine root biomass (Karnosky et al. 2005). Carbon inputs to the Aspen FACE soils were increased under elevated CO_2 as seen by the increase in soil respiration. However, under the combination of elevated CO_2 + ozone, stable soil carbon formation was decreased by 50% compared to that under elevated CO_2 alone (Loya et al. 2003). This suggests that NPP-induced changes in the atmosphere may have a significant impact on the formation of stable soil carbon (Karnosky et al. 2005).

6.4 Conclusions

This chapter has briefly reviewed the history and evolution of scientific understanding of the effects of sulfur, nitrogen, mercury, other heavy metals, ozone, and organic air pollutants on ecosystems. Acid deposition and ozone effects were well studied in the 1980s, and this work helped form the scientific basis for legislation such as the Clean Air Act Amendments of 1990 in the United States and various federal-provincial agreements in Canada. In contrast, there were fewer studies in Mexico during the 1980s, though recent work has demonstrated that air pollutants cause ecosystem stress in this region as well, particularly in the Valley of Mexico.

The ecosystem effects and focus of studies are somewhat different in the arid and semi-arid climate that dominates much of Mexico and the western United States compared with work in eastern North America. For example, in the western United States, researchers have shown impacts of nitrogen deposition on alpine vegetation, aquatic diatoms, and semi-arid shrubs, whereas work in eastern North America has focused more strongly on the effects of acidification on aquatic biological organisms such as fish and invertebrates.

Study of the effects of atmospheric mercury deposition on ecosystems reflects a more complex problem compared to that of sulfur. Reliable measurements of low levels of mercury in the environment were only first achieved in the 1990s, and scientists are still attempting to quantify the rates of mercury transformation processes and the availability and mobility of various pools of mercury in ecosystems. The less developed state of mercury science is reflected in the earlier stage of development of accurate models of the mercury cycle compared to the better established sulfur/nitrogen cycling models such as MAGIC and PnET-BGC that are used in the acidification modeling communities. The biogeochemical cycling of nitrogen is also complex and difficult to model accurately despite a long history of modeling the fate of nitrogen that dates to the 1980s in the atmospheric deposition effects research community.

The broad picture across North America from the 1980s to today is that sulfur, oxidized nitrogen species (NO_x), and mercury deposition, as well as ozone levels, are generally decreasing (see also Chap. 12). However, many important exceptions to this generalization include increasing NO_x deposition across much of western

North America, and stable or increasing ammonium deposition throughout North America. Additionally, evidence indicates that intercontinental transport and deposition of mercury is increasing, especially from Asia to North America, a pattern that is likely to continue. These trends are recognized because of several well-established networks that monitor wet and dry deposition of nitrogen and sulfur such as CAPMoN in Canada, and NTN and CASTNET in the United States. Trends are more difficult to evaluate in Mexico because of the relatively recent development of monitoring networks for atmospheric deposition. Moreover, another land-use issue, deforestation is a very important factor in Mexico, further complicating a clear understanding of air pollution effects. The greater ability of scientists to document air quality-related trends in the United States and Canada than in Mexico further emphasizes the value of long-term monitoring networks that can document the success of past and current air quality policies and guide decisions about future policies.

As atmospheric deposition of sulfur and nitrogen have declined since the 1980s across large parts of North America, there have been parallel increasing trends in pH and ANC in many monitored waters. These trends, however, which are consistent with the beginnings of ecosystem recovery from acidification, are not as great as the declines in precipitation acidity, reflecting lags in these systems. Long-term base cation depletion from soils has been invoked as a likely reason for weak correlations between decreases in the acidity of atmospheric deposition and key aquatic ecosystem indicators such as pH and aluminum concentrations, and an increasing body of evidence supports the pivotal role of base cation depletion in delaying ecosystem recovery in senstive regions.

Monitoring in the United States and Canada has mainly focused on surface-water chemistry, and unfortunately, few long-term data sets exist to evaluate current trends in soil indicators such as soil base saturation. We note also that the lack of long-term repeated monitoring of soil chemistry is a limitation to the accuracy of models that predict future surface-water chemistry because these models must now rely on few data points and must make unconstrained assumptions of the changes in soil chemistry over time. There has also been little long-term and consistent monitoring of aquatic and terrestrial biota to evaluate recovery trends in sensitive ecosystems. The few studies available indicate little biological recovery to date and suggest that recovery may lag decades behind the recovery of biologically-relevant water chemical parameters.

A number of studies by the agricultural research communities in the United States are currently underway to study the effects of air pollution on managed (farm) ecosystems, especially on the effects of ozone which tends to lower crop yields (e.g. Krupa et al. 2000). In the United States and Canada, mitigation of air pollution effects to crops is generally addressed by modified plant varieties and by changes in soil management, such as increased liming in acidifed regions. The situation in Mexico is a bit different, as a number of studies have linked air pollution to crop damage, especially near urban and industrial sources, but work does not seem to be as advanced in the selection of cultivars which better resist ozone effects.

6.5 Recommendations for Accountability and MultiPollutant Interactions

The purpose of this assessment was to describe air pollutant effects on ecosystems and to evaluate the current state of accountability systems that evaluate air pollutant impacts on ecosystems, and to also highlight multipollutant interactions that may justify new strategies for controlling air pollutant emissions in the future. Below, we summarize some key recommendations pertinent to these objectives.

6.5.1 Accountability for Assessing Air Pollutant Effects on Ecosystems

- The current networks for evaluating atmospheric deposition of sulfur, nitrogen, are adequate in the United States and eastern Canada and should be maintained for evaluating the effects of future air quality policies. However, neither the CASTNET nor the CAPMoN networks in the United States and Canada measure concentrations of ammonia as well as those of certain other nitrogen species, and dry deposition of nitrogen is therefore probably being underestimated by these networks. With an increasing emphasis on nitrogen deposition as an issue for forests and aquatic systems, this is a shortcoming in need of attention in all three countries covered by this review. Another improvement would be to develop near-real-time measurement of key parameters to allow the study of climatic, meteorological or depositional events. A more robust and extensive dry deposition network in Mexico would be helpful in better evaluating the environmental effects of air pollutant deposition. Currently, Mexico has a dry deposition network that covers only the largest urban area (Mexico City) and does not extend into important ecosystems located further away (SIMAT-REDDA http://www.sma.df.gob.mx/simat/consultas.htm.).
- Existing monitoring networks could be enhanced by leveraging the resources of new programs designed to monitor ecosystems that might use similar methods and make similar measurements to those of the existing networks. Where feasible, new monitoring programs should consider enhancing existing monitoring networks with additional sites as well as co-locating new types of monitoring that might enhance existing efforts such as NADP, LTM/TIME and CAPMoN.
- Networks for evaluating mercury deposition have a short history, but have grown rapidly to reflect increasing concern about the ubiquitous problem of elevated levels of mercury in fish throughout North America. As these networks such as MDN in the United States continue to grow, attention should also focus on maintaining the sites with the longest data records to better evaluate trends through time. Canada currently has poor geographic coverage of mercury deposition sampling stations. Before a large scale analysis of environmental mercury deposition in Canada can be done, a much better spatial representation of deposition patterns is necessary. Moreover, it is essential that atmospheric monitoring sites

are located in regions where ecosystem monitoring and research are being undertaken in order to most efficiently use available resouces.

- The lack of networks in North America to monitor dry deposition of mercury, as well as acids and other pollutants is a concern. Recent studies have shown that dry deposition of mercury is about 60–80% of the annual new input of mercury to forested ecosystems, a greater proportion than has been measured for sulfur and nitrogen. The nascent dry deposition network developing through the National Atmospheric Deposition Program is an encouraging sign for developing better data on geographic variation, but a lack of financial resources may hamper this effort. The same situation exists in Canada while the situation in Mexico is also in need of major improvement.
- Current monitoring of the effects of mercury deposition on ecosystems is haphazard and lacking uniformity across geographic regions, which poses a challenge to providing an accurate picture of the current pattern of ecosystem effects across the United States For example, each state collects its own data on fish mercury concentrations, and a wide range of sampling frequencies and intensities currently exists. Additionally, most states do not momitor waters for mercury chemistry on a routine basis. In both Canada and the United States, government-university partnerships are attempting to improve this situation by developing nationwide programs with unifirm methods and quality control protocols.
- A thorough analysis of the current effects of atmospheric acid deposition on terrestrial ecosystems, and an assessment of whether the ecosystems are recovering from recent reductions in acid deposition rates is hindered by a lack of long-term monitoring of terrestrial ecosystems, including soils and vegetation.
- Good surface water monitoring programs measure acid deposition related surface water chemistry across eastern Canada and the United States and these should be maintained. However, existing networks to evaluate aquatic biota, forest and forest soil trends are not well developed and need to be strengthened. It is important that enhanced biota and soil monitoring not come at the expense of existing surface water chemistry monitoring networks because these are currently the only long-term continuous records for evaluating acid deposition effects.
- Evaluation of the acidification status of ecosystems has relied heavily on measurements of ANC and could be improved with additional indices based on Al and Ca concentrations in soils and waters, because ANC values are affected by natural organic acids. Broader evaluations of ecosystem recovery that fully consider a wider array of chemical indicators need to be adopted.
- A critical loads approach has been used as a tool to assess the effects of emission reductions on Canadian ecosystems by federal and provincial policy makers. This approach has been used in a more informal and indirect manner in the United States, which reflects the language and regulatory approach of the Clean Air Act. Some limited applications of a direct critical loads approach are beginning to appear, mostly by federal land management agencies such as the National Park Service and the U.S. Forest Service, and this approach has the potential to be more widely applied in the United States to inform an ecosystem-relevant approach to managing air pollutant emissions. Federal agencies in the United

States that include EPA, NPS, and USFS are attempting to address the lack of comprehensive critical loads information by funding several studies that will provide future information to policy makers.

Links between ecosystem scientists and the operators of atmospheric monitoring networks must be strengthened to ensure that information regarding atmospheric pollutant inputs are better linked to outcomes in environmental systems. Moreover, joint studies between the two disciplines should be encouraged; faster turnaround times for atmospheric data analysis and quality control would greatly assist ecologists and geochemists.

6.5.2 Multipollutant Effects on Ecosystems

- The combined effects of sulfur and nitrogen deposition on ecosystem acidification have been known, studied, and applied since the 1980s. The combined consideration of sulfur and nitrogen in the US Clean Air Act and in air quality legislation in Canada, and the science that supported this multipollutant treatment provides an excellent case study of applying a multipollutant approach to air quality management. However, one piece of the multipollutant puzzle, for sulfur and nitrogen deposition, is missing. Ammonium concentrations have been increasing recently in many parts of North America. The principal source of this ammonium is likely from agriculture, and this source of emissions is not currently regulated by air pollutant policies in North America. Better characterization of the emissions sources and deposition patterns of ammonium and ammonia is needed. A current effort to use passive ammonia samplers at a select group of CASTNET and NADP sites as well as in southern Ontario will help to better characterize geographic patterns of ammonia deposition. This effort should be supported and possibly expanded to include a greater number of sites in the future.
- As climate change models improve, and as geochemical and ecological impacts are better understood, it should become possible to develop models of air pollutant effects on ecosystems with likely changes in climate and the carbon cycle. We recognize that these effects are complex and not completely understood today, but consideration of climate change trends is needed to provide a range of uncertainty in future predictions about air pollutant effects.
- Recent research has highlighted the role of atmospheric sulfur deposition and of pH in mercury methylation and uptake into fish and other biota. These research results suggest that controls on sulfur emissions (and probably nitrogen emissions as well) may be used in part to assist with reducing environmental mercury contamination.

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Chapter 7
Atmospheric Science of Air Pollution Phenomena—Current Directions Toward Exposure Characterization

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The rationale and success of an approach to multipollutant air quality management must consider the chemical transformation and fate of the relevant pollutant species that affect health and welfare outcomes. The chemical and physical processes that determine pollutant lifetimes also govern the transport of these substances, their disposition, and consequently their ultimate fate in the environment. Air quality models (discussed in Chap. 9) play a critical role in the development of mitigation strategies for addressing the ozone and $PM_{2.5}$ NAAQS and acid deposition. The quality of these mitigation strategies depends on an accurate depiction of the chemical and physical transformation processes associated with these pollutants and their respective precursors and in turn quantify their source to receptor relationship. This chapter illustrates that ozone, $PM_{2.5}$ and acid deposition have common precursors (and thus emission sources) and transformation processes. In addition, their comparable lifetimes result in similar transport and regional distribution patterns.

The extension of air quality models to a broader mix of pollutants (e.g., hazardous air pollutants [HAPs] or the chemical composition and size distribution of PM) requires continually improved characterization of the chemical and physical transformations of these compounds, their relevant precursors, and their lifetimes in time and space. The chapter provides insights as to those processes most likely to affect this broad mix of pollutants in terms of their distribution on the urban/regional and the local scale (i.e., tens to hundreds of meters from a source).

A viable multipollutant air quality management approach must provide a credible account of the chemical and physical transformation processes in linking sources to receptors. As such, demonstrating the efficacy of atmospheric transformation processes in observation- and emission-based air quality models is a key element in tracking the progress and effectiveness of pollutant mitigation strategies and is essential in demonstrating accountability in the air quality management system.

Atmospheric chemistry plays yet another very important role in the multipollutant paradigm. Elucidating the details of the chemical and physical transformation

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processes associated with atmospheric pollutants provides insight to the variety of chemical reaction products and transient species present in the atmosphere that may participate as active agents effecting health or ecosystem outcomes and which in combination may pose a more potent threat. Although such synergisms remain to be demonstrated, detailed characterizations of the chemical and physical processes occurring in the atmosphere can provide insights as to hypothesis testing and identification. The demonstration of synergistic effects on outcomes would contribute significantly to the multipollutant concept and further progress in closing the accountability chain.

The knowledge of the chemical transformations associated with photochemical oxidants, acid bearing species, and particulate matter has evolved over the past four decades, with the longest record of scientific inquiry associated with photochemical oxidants. The NARSTO Assessments on ozone (NARSTO 2000) and particulate matter (McMurry et al. 2004), reviews by the National Research Council (NRC 1991, 1998, 2004a, b), and the EPA Criteria Documents (EPA 2006) have provided an evolving state-of-the-science assessment of the chemistry of polluted atmospheres. It is not the intent of this chapter to provide another comprehensive review of the chemistry of the atmosphere, but to provide an overview highlighting the atmospheric processes most significant in considering a multipollutant air quality management paradigm and the challenges therein.

7.1 Overview of Atmospheric Chemical Transformation Processes

Chemical transformations associated with photochemical oxidation of volatile organic compounds and oxides of nitrogen have been schematically depicted (see Fig. 7.1) over the years by chain reactions that involve free radical intermediates, mainly hydroperoxy (HO_2), hydroxyl (OH), organo-peroxy (RO_2) and organo-oxy (RO) (where R in RO_2 and RO can be any volatile organic entity). These radical reactions drive the oxidation of the primary emitted precursor species noted by diamond shapes in Fig. 7.1, while transient photochemical oxidation products are noted by hexagonal shapes and more stable products listed below the figure. Nitrogen dioxide (NO_2) formation from the peroxy radical (HO_2 and RO_2) oxidation of nitric oxide (NO) undergoes photolysis in sunlight to regenerate nitric oxide and to form oxygen atoms (O^3P) that react predominantly with oxygen to form ozone. The chemical reactivity of VOCs (i.e., the chemical kinetic rate of reaction, typically expressed with respect to hydroxyl radical (OH), and subsequent radical producing potential) along with the ratio VOC to NO_x and their respective atmospheric concentrations are important parameters in the ozone forming potential of polluted atmospheres. These parameters in conjunction with solar intensity (and temperature to a lesser extent) drive the chain reaction cycle (chain length) as illustrated by the red arrows in Fig. 7.1, which drive up the NO_2/NO ratio and subsequently the production of ozone. The reaction chain length (i.e., radical propagation rate/radical

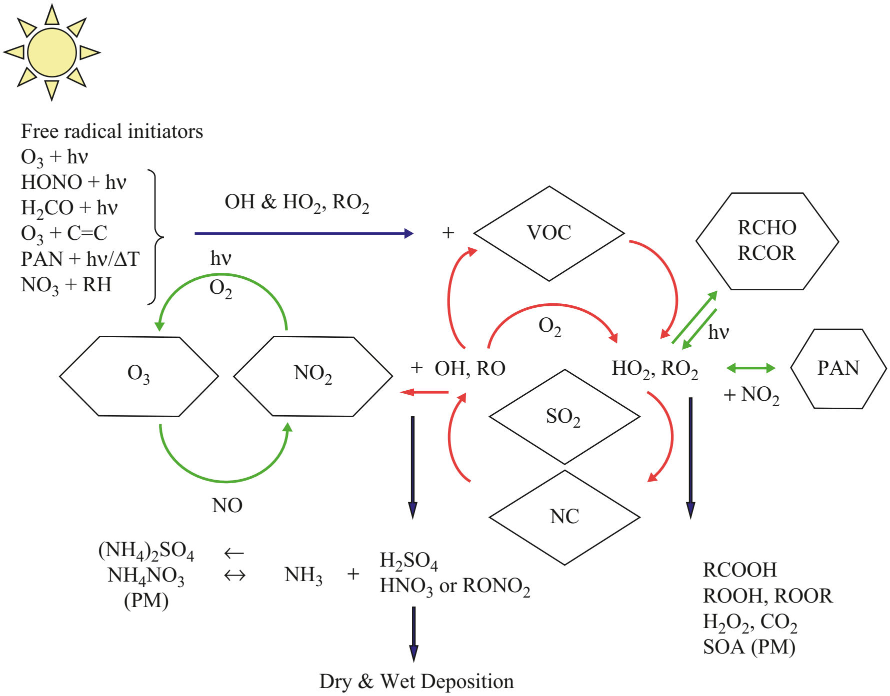

Fig. 7.1 Schematic of the atmospheric photochemical oxidation cycle

termination rate) is modulated in part by free radical initiators and free radical sinks as illustrated by the blue arrows in Fig. 7.1.

These same free radicals play an important role in the secondary production of inorganic and organic particulate matter. Figure 7.1 illustrates the major inorganic pathways for production of secondary PM as NH_4NO_3 and $(NH_4)_2SO_4$, where atmospheric nitric and sulfuric acids form predominantly under sunlight conditions from the reaction of OH with NO_2 and SO_2 respectively and are subsequently neutralized by their reaction with ambient ammonia (NH_3) and other basic constituents. Depending on the magnitude of the acid forming step and the neutralizing capacity of the atmosphere (e.g. NH_3 concentration, alkalinity of ambient aerosols) the particulate matter may exhibit acidity during high particle production events typically associated with high photochemical oxidation (Schwab et al. 2004; Liu et al. 1996; Koutrakis et al. 1988). The details of the transformation of VOC to secondary organic aerosol (SOA) in the atmosphere are very complex. The field has recently undergone a renaissance as a result of the renewed interest in fine particulate matter and its associated health effects. More detailed discussions of the chemistry of nitrogen oxides and SOA are presented in Text Boxes 7.3 and 7.4.

It is clear from Fig. 7.1 that air quality outcomes associated with ozone, particulate matter, and acid precipitation share common gas phase transformation processes. Not illustrated in Fig. 7.1 are a host of heterogeneous reactions known to occur in liquid water media present in cloud/fog droplets, aerosols and on wetted surfaces (Jacob 2000). The quantification of these heterogeneous reactions and their ultimate contributions to atmospheric chemical transformations is critically tied to quantifying the liquid water content of these entities in the atmosphere. Cloud processes contribute significantly to the oxidation of SO_2 via heterogeneous reactions with ozone and hydrogen peroxide under summer and winter conditions. Providing measurements to evaluate the performance of models in predicting these heterogeneous contributions remains one of the major challenges to the air quality measurement and modeling communities. It should be noted that predictions of cloud presence, fractional cover, depth, and liquid water content are all products of the meteorological models that drive the chemical transport models. Quantifying these parameters is as essential as the treatment of the heterogeneous chemical reactions. The prediction of cloud properties remains a major challenge in the modeling of global climate change and will likely be one of the critical links in coupling climate change impacts to air quality futures (see Chap. 11).

The chemical details of the generic cycles illustrated in Fig. 7.1 have evolved significantly since the 1970s. These improvements have included laboratory determinations of chemical kinetic rate constants for hundreds of inorganic and organic species of atmospheric relevance. Reviews of rate constants are compiled and evaluated on a periodic basis (e.g., Sander et al. 2007; Atkinson et al. 2004, 2007). Mechanistic characterizations of atmospheric chemistry have evolved based on the development of the explicit treatment of the relevant chemical reaction steps and their implicit aggregation for use in operational air quality simulation models. Explicit treatments have resulted in the development of master chemical kinetic mechanisms, which consider thousands of chemical species and reactions (Madronich and Calvert 1990; Jenkin et al. 1997; Derwent et al. 2007) of relevance in the atmosphere. Explicit reaction mechanisms have served as a test bed for developing subsets of specific reactions as well as parameterizations of generalized classes and/or groupings of the myriad of volatile organic compounds present in the atmosphere. These surrogate chemical mechanisms strive to capture the essential features of the atmospheric chemical transformation processes and have evolved predominantly through comparisons with thousands of smog chamber studies (Yarwood et al. 2005; Dodge 2000; Stockwell et al. 1997; Gery et al. 1989) of the chemical compounds considered most relevant to the formation of photochemical oxidants in the atmosphere.

The importance of biogenic emissions (organic biogenic compounds in particular) in regional ozone production (Trainer et al. 1987; Barket et al. 2004; Warneke et al. 2004) and more recently their role in the formation of secondary organic aerosols (Odum et al. 1996; Nenes et al. 1999; Griffin et al. 2002; Claeys et al. 2004; Lane and Pandis 2007) reflect some of the mechanism enhancements that are in development. This new knowledge is being incorporated into the mechanisms used in next generation air quality simulation models and will better inform the air quality management process in the development of multipollutant mitigation control strategies. These chemical transformation mechanisms link VOC, NO_x, SO_2 and NH_3 precursors to ozone, $PM_{2.5}$ mass and its major constituents (i.e., ammonium, sulfate, nitrate and organic), and although these chemical mechanisms remain to be evaluated and tested with respect to their prognostic capabilities, they are capable of providing multipollutant precursor mitigation strategies for series of air quality/environmental endpoints (e.g., ozone, $PM_{2.5}$ mass, acid deposition and regional haze [visibility impairment]). As with ozone, retrospective studies of particulate matter are limited by the availability of emission trends and air monitoring data sets of the relevant precursor species. These limitations are discussed in some detail in Chaps. 4 and 10 and must be addressed if the models are to meet the expectations of air quality managers. The lowering of the $PM_{2.5}$ 24-h standard and the anticipated lowering of the 8-h ozone standard both present further challenges to the precision and accuracy of models, which in turn place more demands on the precision and accuracy of the chemical mechanisms that link precursor transformations to air quality endpoints. Similar to the ozone/precursor trend analysis case study discussed in Chap. 12, tracking the contribution of secondary organic aerosol to $PM_{2.5}$ mass and the repartitioning of PM sulfates and nitrates with changing NH_3 and SO_2 emission scenarios remains a significant challenge to the emission and air monitoring communities.

7.2 Chemical Transformation Involving HAPs and Non-criteria Pollutants

Hundreds of air contaminants may be harmful to human health, including the 187 hazardous air pollutants (HAPs) listed by EPA and similar lists complied by Canada and Mexico (see the List of Terms). Many of these compounds are emitted directly into the atmosphere, and their emission sources have been identified (U.S. National Emission Standards for Hazardous Air Pollutants [NESHAP]; http://www.epa.gov/ttn/atw/mactfnlalph.html). In addition, many HAPs are VOC precursors that contribute to the formation of ozone through their chemical oxidation and $PM_{2.5}$ through secondary organic aerosol formation. Specific HAPs are formed by chemical reactions involving ubiquitous precursor compounds found in the atmosphere as a result of emissions from anthropogenic and biogenic sources. HAPs can undergo chemical reactions that convert highly toxic substances to less toxic or inert products as well as convert relatively inert substances to more toxic substances. Exposure to HAPs occurs on time and space scales that range from seconds (tens of meters) to days (tens of kilometers) governed by the configuration of their sources and chemical and physical processes affecting their atmospheric lifetimes.

Hazardous air pollutant exposure modeling must consider approaches for characterizing the chemical and physical properties and estimating their source of origin. For example, Table 7.1 shows a partial list of HAPS categorized by physical and chemical properties; Table 7.2 shows a scheme for classifying HAPS by reactivity categories based on associated reaction rates of a subset of the species (Rosenbaum et al. 1999).

Reactions involving the formation and removal of organic HAPs in the atmosphere are generally associated with OH and NO_3 radicals and to a lesser extent with O_3 for some unsaturated anthropogenic and biogenic chemical compounds. Table 7.2 shows a classification scheme within reactivity categories for the removal of organic HAPs (and selected precursors) based on their reaction rate constants with OH, NO_3 and O_3. The time and space scales of HAPs primary and secondary

Table 7.1 Sample subset of the physical and chemical properties of HAPs. (Source: Rosenbaum et al. 1999)

HAP	Formula	G/P[a]	O/I[b]	Reactive[c]	Secondary[d]
Acetaldehyde	CH_3CHO	G	O	M	Y
Acetamide	CH_3CONH_2	G	O	H	P
Acetonitrile	CH_3CN	G	O	VL	
Acetophenone	$C_6H_5COCH_3$	G	O	L	P
Acetylaminofluorene	$C_{13}H_8NH_2COCH_3$	G/P	O	H	
Acrolein	CH_2CHCHO	G	O	M	Y
Acrylamide	$CH_2CHCONH_2$	G	O	H	
Acrylic acid	CH_2CHCO_2H	G	O	M	P
Acrylonitrile	CH_2CHCN	G	O	L	
Allyl chloride	CH_2CHCH_2Cl	G	O	M	
Aminobiphenyl	$C_6H_5C_6H_4NH_2$	G	O	H	
Aniline	$C_6H_5NH_2$	G	O	H	
Antimony compounds	Sb	G/P	I	L	
Arsenic compounds	As	G/P	I	L	
Asbestos	$Mg(Si_4O_{10})(OH)_8$	P	I	L	
Benzene	C_6H	G	O	L	
Etc.					

[a] G/P refers to gas or particle phase

[b] O/I refers to organic or inorganic compound

[c] Reactivity is H(high, $\tau < 6$ h), M(medium, $\tau = 6$–24 h), L(low, $\tau = 1$–60 days) or VL(very low, $\tau > 60$ days);

[d] Secondary refers to Y(formed by secondary atmospheric reactions), P(possibly formed by secondary atmospheric reactions)

Table 7.2 Reactivity categories and associated rate constants. (Source: Adapted from Rosenbaum et al. 1999)

Category	Typical hazardous air pollutant	k_{OH} (ppt^{-1} s^{-1})	k_{NO_3} (ppt^{-1} s^{-1})	k_{O_3} (ppt^{-1} s^{-1})
Very high	Acetaldehyde precursor, 1,3-butadiene, cresol, MEK precursor, propionaldehyde precursor	1.4E-3	2.4E-6	1.4E-9
High	Aniline	2.4E-3	0	0
Medium high	Chloroprene, formaldehyde precursor, maleic anhydride	9.6E-4	0	1.4E-10
Medium	*Acetaldehyde, acrolein, formaldehyde, MIBK*, naphthalene, phenol, *propionaldehyde*, xylene	4.8E-4	0	
Medium low	Ethylbenzene, glycol ethers, toluene, vinylidene chloride	1.9E-4	0	
Low	Cumene, ethylene gycol, hexane, biphenyl, *methyl ethyl ketone*, tetrachloroethylene, 1,1,2-trichloroethane, trichloroethylene, vinyl bromide	9.5E-5		

Compounds in italics are photo-active, with photolytic rate constants that are season and latitude dependent formation processes will be important in defining multipollutant exposure environments and effective mitigation strategies.

The secondary production of HAPs can be quite important in the atmosphere and estimates of the major and minor precursor sources for two groups of selected compounds—those exhibiting a substantial contribution for secondary formation processes and those that make only a minor contribution—are presented in Table 7.3.

Our knowledge of the atmospheric chemistry of HAPs and their associated precursors is incomplete, and as a result the current generation exposure models do not explicitly treat the chemical and physical transformation processes associated with HAPs. Exposure models for HAPs (e.g. ASPEN) have rather simplistic first order treatments for the formation and loss of HAPs based on estimates of the concentration of the secondary HAPs as the difference between the modeled precursor concentrations in the inert mode and their concentrations considering reactive decay. HAPs exposure models are discussed in Chap. 9.

The treatment of air toxics within chemical transport models (Seigneur et al. 2002) is in its early stages and future progress will very much depend on the availability of quality emission inventories and observations from measurement networks to develop and evaluate these modeling systems. However, the mechanisms

Table 7.3 Major and minor precursor sources for hazardous air pollutants. (Source: Rosenbaum et al. 1999)

Hazardous air pollutant	Major precursors	Minor precursors
HAPS for which secondary formation may be a major or only source		
Acetaldehyde	Propene, 2-butene	Numerous
Acrolein	1,3-Butadiene	Other 1,3-dienes
Carbonyl sulfide	Carbon disulfide	
Cresol	Toluene	
DDE	DDT	
Formaldehyde	Ethene, propene, isoprene	Numerous
Hydrochloric acid	Nitric acid, chlorinated VOC_x	
Methyl ethyl ketone (MEK)	2-Methyl-1-butene, butane, 2-butene, 3-methyl pentane, isoprene	
N-nitroso-N-methylurea	N-methylurea	
N-nitrosodimethylamine	Dimethylamine	Trimethylamine
N-nitrosomorpholine	Morpholine	
Phosgene	Tetrachloroethylene, trichloroethylene, vinylidene chloride	Other chlorinated alkenes and alkanes
Propionaldehyde	1-Butene	Numerous
HAPS for which secondary formation may be a minor source		
Maleic anhydride	Toluene, o-xylene	Benzene
Methanol	2-Butene	
Methyl isobutyl ketone	2,4-Dimethyl-1-pentene	
Nitrobenzene	Benzene	
4-Nitrophenol	Phenol, nitrobenzene	
Phenol	Benzene	
2,4,5-Trichlorophenol	2,4,5-T	

for many VOCs identified in photochemical oxidant models do provide basic insight into the production and loss of some HAPs in the atmosphere, for example, formaldehyde as discussed in Text Box 7.1. Another important air toxic is mercury which has been found to have a complex chemistry linked with the atmospheric oxidation cycle (Text Box 7.2). Mercury chemistry is partially known, and is modeled as a global and local pollutant (see also Chapter 11).

Text Box 7.1 The Case of Formaldehyde—Multipollutant Linkage Ozone—HAPs

The atmospheric chemistry of formaldehyde is well understood and its formation and loss reactions are pivotal to the VOC/NO_x oxidation processes leading to photochemical ozone formation. Most VOCs undergoing oxidation in the atmosphere produce formaldehyde as an intermediate product. Formaldehyde has also been accounted for in source profiles of exhaust emissions from gasoline and diesel engines and industrial processes. Source emission estimates of formaldehyde based on the 1996 National Air Toxics Study (NATS) indicate that mobile sources are a major contributor (Fig. 7.2). It should be noted that mobile sources also contribute precursor hydrocarbons (alkenes and alkanes mainly) which undergo photochemical oxidation resulting in the formation of formaldehyde (e.g. Harley and Cass 1994 have suggested that >75% of the summertime modeled formaldehyde concentrations in Los Angeles are due to secondary production). Similar transformation processes can occur with biogenic hydrocarbons, which are sources of formaldehyde in rural regions with significant biomass (Palmer et al. 2006). Ambient exposures to formaldehyde occur on multiple space scales. Acute exposures occur predominantly near major sources (e.g. highways or during photochemical oxidant episodes), while chronic exposures occur on urban and regional scales during photolytic periods and may be significantly influenced on the regional scale by biogenic emissions. Figure 7.3 shows formaldehyde comparison results from the air toxics version of the Comprehensive Air Quality Model with Extension (CAMx) (ENVIRON 2002), from the California MATES-II study. Figure 7.4 shows formaldehyde concentrations as predicted by a mesoscale meteorological-air quality modeling system (Cai et al. 2008).

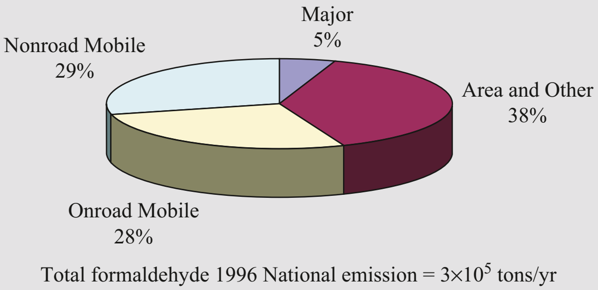

Fig. 7.2 National 1996 formaldehyde emissions by source type

CAMx-Tox MATES-II Formaldehyde

	UAM-Tox EMFAC7G	**CAMx EMFAC7G**	**CAMx EMFAC2000**
N	502	502	502
Average Observed (μg/m^3)	4.8413	4.8413	4.8413
Average Predicted (μg/m^3)	3.3549	7.4321	9.1052
Bias (μg/m^3)	–1.4864	2.5908	4.2639
Gross Error (μg/m^3)	2.6984	4.0573	5.2589
RMSE (μg/m^3)	3.5861	5.4102	6.9849
Fractional Bias (%)	–25.5018	44.9967	60.5307
Fractional Error (%)	64.1063	67.8014	75.2718
Normalized Bias (%)	155.0187	427.9297	576.5912
Normalized Error (%)	218.2940	445.3301	588.2816

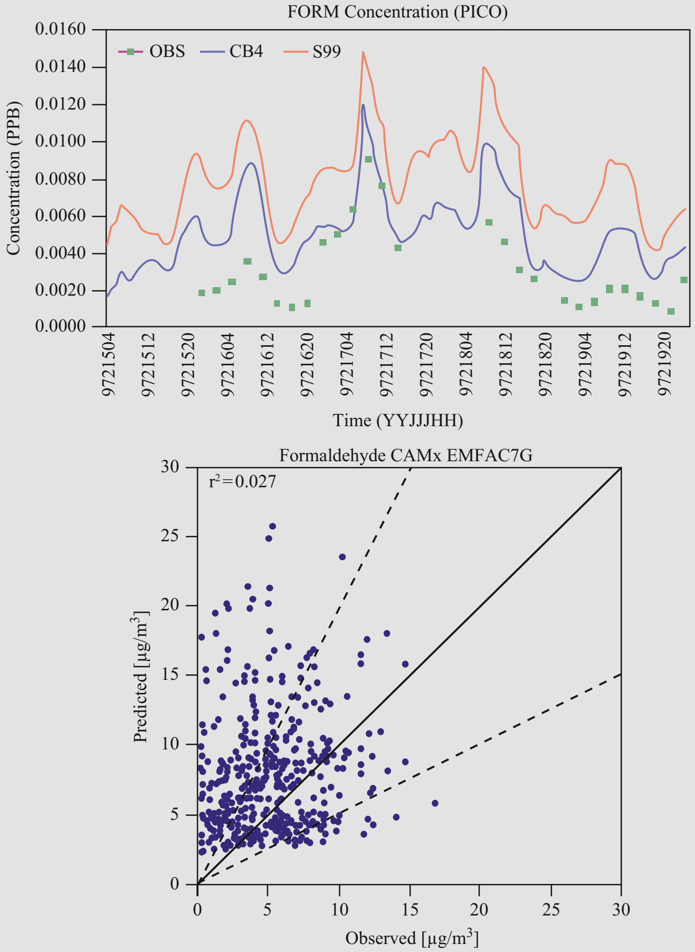

Fig. 7.3 CAMx model versus observed formaldehyde concentrations from California MATES-II study. (ENVIRON Final Report CRC Project A-42-2, 2002)

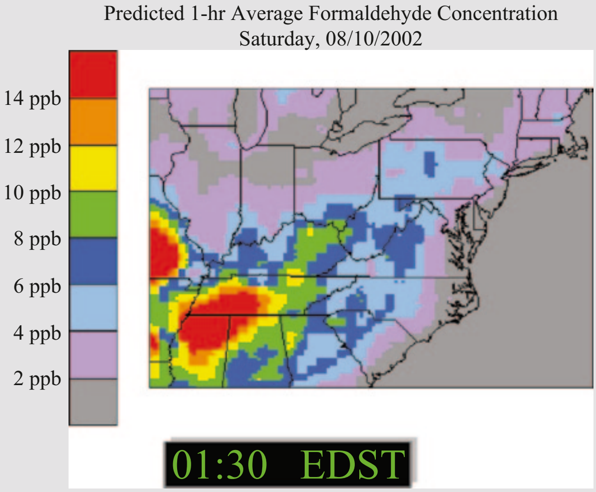

Fig. 7.4 Forecasted formaldehyde concentrations from a coupled mesoscale meteorological/air quality modeling system**.** Note—modeling studies suggest that roughly 80% of ambient formaldehyde in summer and 30% in winter is secondary. (Ligocki et al. 1991; Harley and Cass 1994)

Text Box 7.2 Mercury Chemistry

Mercury is present in several forms in the atmosphere. Overall, most of atmospheric mercury is gaseous elemental mercury, Hg^0 (>95%), with some amount of gaseous divalent mercury, Hg^{II} (also referred to as reactive gaseous mercury or RGM, which includes $HgCl_2$, $Hg(OH)_2$, HgO and other species), and particulate mercury species that include non-volatile species (HgS), semi-volatile species (HgO) and adsorbed Hg^{II} species. Near some anthropogenic sources, the relative fraction of Hg^{II} can be more significant. The overall atmospheric lifetime of mercury (regardless of its oxidation state) is less than one year; the atmospheric chemical lifetimes of individual mercury species are less and several reduction–oxidation (red–ox) cycles may occur before mercury is removed from the atmosphere by dry or wet processes. Figure 7.5 depicts the major known reaction pathways of atmospheric mercury. Hg^0 is oxidized to Hg^{II} in the gas phase and in the aqueous phase by oxidants such as ozone, hydroxide, and bromine radicals (Br and BrO). Hg^{II} is reduced to Hg^0 in the aqueous phase by dissolved SO_2 and possibly by some photochemical species. There is also some empirical evidence of Hg^{II} reduction in coal-fired power plant plumes, although this potential reaction pathway needs to be confirmed. This summary of mercury chemistry highlights the fact that the mercury redox cycle is influenced by photochemical oxidants, SO_2 and PM concentrations (Lindberg et al. 2007).

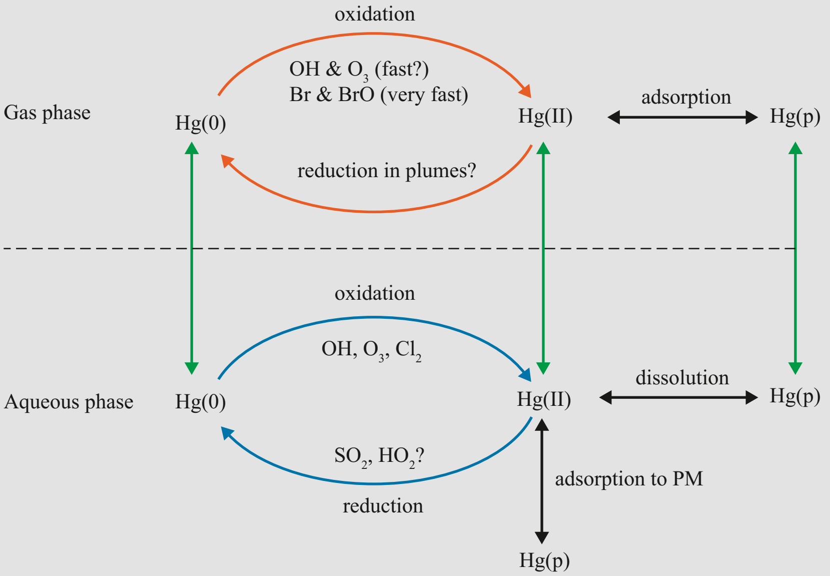

Fig. 7.5 Major reaction pathways of atmospheric mercury

As discussed in Sect. 7.1, current ozone air quality simulation models do not explicitly treat the chemical reactions of the hundreds of volatile organic compounds identified in source specific emission profiles. This holds true for PM models as well, where the production of secondary organic aerosols (see Text Box 7.3) have also been parameterized. One obvious opportunity for the development of a multipollutant modeling system would be to explicitly treat each compound identified in source specific emission profiles. Such multipollutant model systems will prove to be computationally challenging, but not impossible given today's computing resources. Measurement programs to study and evaluate the linkage between VOC precursors and ozone, primary and secondary organic PM and primary and secondary air toxic compounds in the atmosphere may prove the more daunting task.

Text Box 7.3 Secondary Organic Aerosols

The formation of secondary organic aerosols in the atmosphere is closely tied to the photochemical oxidation processes associated with ozone formation described in Sect. 7.1 and whose reaction pathways are schematically illustrated in Fig 7.1. Organic aerosols found in the atmosphere have both primary and secondary sources. Primary sources can range from condensed lubricating oil to wood smoke, and secondary sources are the result of the oxidation of VOCs from anthropogenic and biogenic sources. The detailed chemical composition of atmospheric organic aerosol remains significantly unidentified (Schauer et al. 1996). It is likely made up of thousands of compounds found in complex mixtures that are made up of primary and secondary components. Only a small fraction of the VOC content of the atmosphere is converted to semi-volatile or non-volatile organic products. The conversion of VOC to organic aerosols was generally thought to be associated with the oxidation of higher molecular weight organic compounds (i.e., substituted aromatics, alkanes with carbon number >7, and biogenic compounds with carbon numbers >5; Griffin et al. 2002; Odum et al. 1996). Although these compounds are significant contributors to SOA formation, it has been observed recently that the photooxidation of smaller organic compounds (e.g. isoprene) can undergo oligomer formation and can contribute significant quantities of SOA to the atmosphere (Claeys et al. 2004; Kroll et al. 2005, 2006; Dommen et al. 2006). The mechanistic details of the chemical transformation resulting in SOA formation remain mostly unresolved, but as previously mentioned the basic atmospheric oxidation processes are thought to hold. The SOA formation pathway represents only a few percent of the available carbon in the atmosphere, but still makes a significant contribution to PM mass in the atmosphere. For example, a 2% conversion of 200 ppbC of NMHC (typical of an urban atmospheric concentration) to SOA results in ~2 μg/m^3 PM carbon. Taking into consideration the oxygen and nitrogen associated with the formation process, PM mass concentration from SOA could range from 2.8 to 3.6 μg/m^3.

Figure 7.1 provides a schematic of the pathways for VOC oxidation in the atmosphere including those processes leading to the formation of semi-volatile and non-volatile organic aerosols. The initial oxidation of a volatile organic compound by OH or other bond breaking constituents almost always results in the formation of an organo-peroxy (RO_2) radical. The predominant pathway for this radical in the presence of NO is to react to form NO_2 and an organo-oxy radical (RO). Depending on the molecular weight and structure of the organic entity (R), it may directly form a carbonyl compound (aldehyde or ketone) or fragment to form a carbonyl compound and organo-peroxy radical, both of lower carbon number than the parent radical. The potential to produce organic aerosol is very much dependent on the molecular weight of the VOC and the partitioning pathway favored by the RO radical. In the case of an NO_x-limiting environment, there are more opportunities for radicals to interact with one another and form higher molecular weight compounds (e.g. organic peroxides, organic acids and hydroxyl substituted carbonyl), which will lead to high yields of SOA formation. Radical association reactions are always potentially available for SOA formation, but will be moderated in high NO_x environments. Figure 7.6 identifies the prominent atmospheric oxidation organo radical pathways where the heavier outlined hexagonal entries are indicative of potential sources of SOA. Although NO_x can lead to significant oxidation and fragmentation of VOCs, as shown here and in Text Box 7.4, organo nitrates can also contribute significantly to SOA as well.

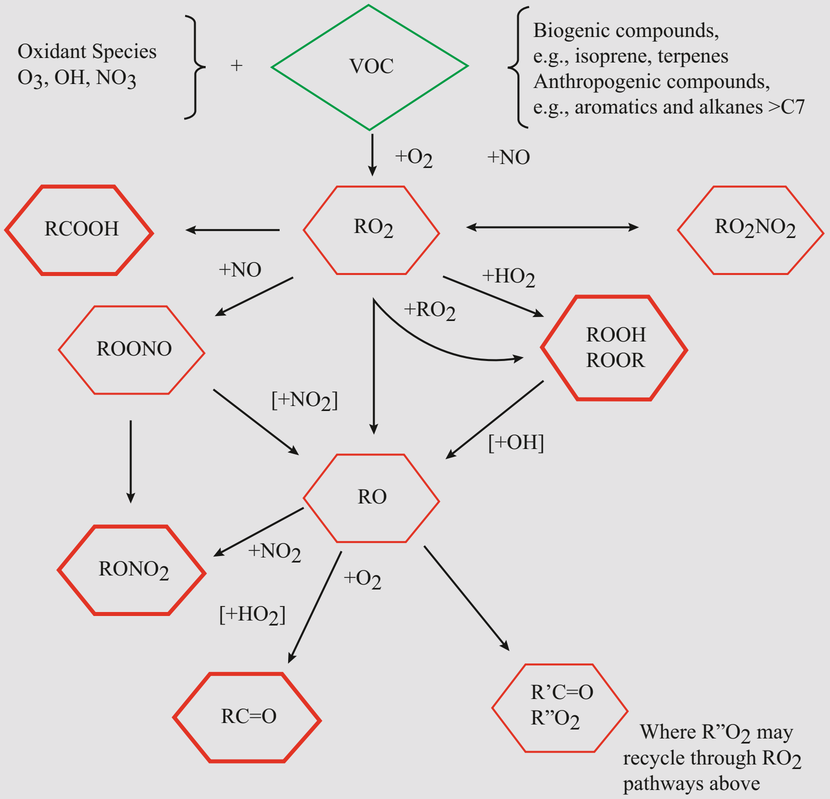

Fig. 7.6 Schematic of the reaction pathways associated with secondary organic aerosol formation in a VOC–NO_x environment. (Adapted from Presto et al. 2005)

7.3 The Role of Chemistry in the Accountability Chain

Chemical mechanisms imbedded in photochemical air quality simulation models must depict the quantitative relationship between VOC and NO_x precursors and ozone formation, in the case of ozone air quality management, and VOC, NO_x, SO_2, and NH_3 precursors in the case of $PM_{2.5}$ air quality management. Tracking and demonstrating the quantitative response of air quality outcomes (e.g., ozone and/or $PM_{2.5}$) to incremental changes in precursor concentrations resulting from regulatory emission controls is a key step in the accountability chain. However, quantitative evaluation of these relationships using observational data remains a challenge. In their most rudimentary form, chemical mechanisms derived to depict the photochemistry of polluted atmospheres have explored the ozone precursor relationship through the so called "Empirical Kinetics Modeling Approach (EKMA) isopleth" diagram (Dodge 1977; NRC 1991; NARSTO 2000). Although rightfully criticized for its simplistic treatment of atmospheric chemistry and dynamics, the surrogate mechanism in theory captures the key reactions representative of the photochemical oxidation cycle involving anthropogenic hydrocarbons and nitrogen oxides and associated reaction chain lengths. As such, EKMA simulations should predict ozone production efficiencies (i.e., an estimate of the number of ozone molecules formed per NO_x molecule consumed) that are testable under selected meteorological conditions.

The failure to make detailed hydrocarbon measurements over the course of historically significant emission changes resulting from developments such as the: (1) introduction of the exhaust catalytic convertor for spark ignition engines; (2) increased volatility of gasoline with the de-leading of gasoline in the 1970s; (3) reductions in gasoline volatility and reactivity with the introduction of reformulated gasoline in the 1990s; and (4) reductions in solvent use, volatility and photochemical reactivity in the 1980–1990s, has proven to be short-sighted and limited our ability to track and provide a detailed accounting of the impact these control programs have had on VOC concentrations over the years. It is generally accepted that hydrocarbon control actions taken based on the EKMA diagram did not achieve the ozone reductions anticipated, and that NO_x controls were needed to effectively mitigate ozone air quality (NRC 1991). The inability to reconcile anthropogenic hydrocarbon emission estimates (mobile source emissions in particular) with ambient observations was seen as a major shortcoming in tracking progress in the management of ozone air quality. The requirement to implement the EPA Photochemical Air Monitoring Stations (PAMS) in ozone non-attainment areas under the 1990 Clean Act Amendments was in response to the NRC (1991) recommendation to address this measurement issue and led to the initial considerations of building accountability into the air quality management process. The EPA PAMS and the Canadian National Air Pollution Surveillance (NAPS) measurement networks provide the opportunity to track trends in ambient concentrations of VOC and NO_x and resultant ozone response within contiguous urban air masses and thus are an essential first step in the chain of accountability in the context of ozone air quality management. Chapter 12 provides an example of this sequence, based on trends in precursor emissions and associated trends in ambient ozone concentrations. Comparative analysis of these example trends suggests that our quantitative understanding of the VOC–NO_x–ozone relationship remains uncertain. Part of this uncertainty may well arise from the disparate spatial distributions over which these precursor reductions have occurred (e.g., NO_x reductions are more associated with elevated point source emissions, while VOC reductions are more associated with ground-level line and area source emissions). Meteorological variability is also a factor, and trend data have been empirically adjusted in attempts to account for factors such as temperature and wind speed. Other factors can be important as well (e.g., cloud cover and precipitation) when estimating ozone production efficiencies from correlations of ozone with NO_y or NO_z measurement data (Trainer et al. 1993; Hayden et al. 2003). The budget species NO_y is a measure of all nitrogen oxide species including NO, NO_2, HNO_3, HNO_2, N_2O_5, NO_3, $RONO_2$ (organic nitrates including peroxyacetyl nitrate [PAN]), and particle NO_3^- and $NO_z = NO_y - NO_x$ (see Text Box 7.4). Because precursor emissions and atmospheric chemistry are so closely coupled by the physical dynamics of the atmosphere, retrospective applications of coupled mesoscale meteorological and chemical transport models constitute the most prudent test of the model's predictive capability (i.e., Δ precursor emission to Δ ozone relationship). Unfortunately, the quantification of precursor emission changes over the past several decades is sufficiently uncertain that testing the trend in the VOC–NO_x precursor-ozone relationship remains problematic.

Text Box 7.4 Chemistry of Nitrogen Oxides

The emissions of oxides of nitrogen (NO_x) serve as another example of a chemical constituent having multipollutant impacts on air quality outcomes. NO_x emissions are directly related to the levels of criteria pollutant NO_2, are critical to the formation of ozone and $PM_{2.5}$ mass (ammonium nitrate and organic nitrates), contribute to the acidification and nitrification of ecosystems through the deposition HNO_3 and particulate NH_4NO_3, and likely contribute to HAP formation through its chemical reactions with organic species in the air environment forming organic nitrates including nitro-PAH, nitroxyketones, nitroxyperoxyalkyl nitrates, alkene glycol dinitrates and nitrosamines.

A schematic of the atmospheric chemistry of nitrogen oxides and key pathways for stable nitrogen product formation is presented in Fig. 7.7. Those compounds within diamond shaped figures have significant source emissions; hexagonal figures represent relatively stable compounds, while those within

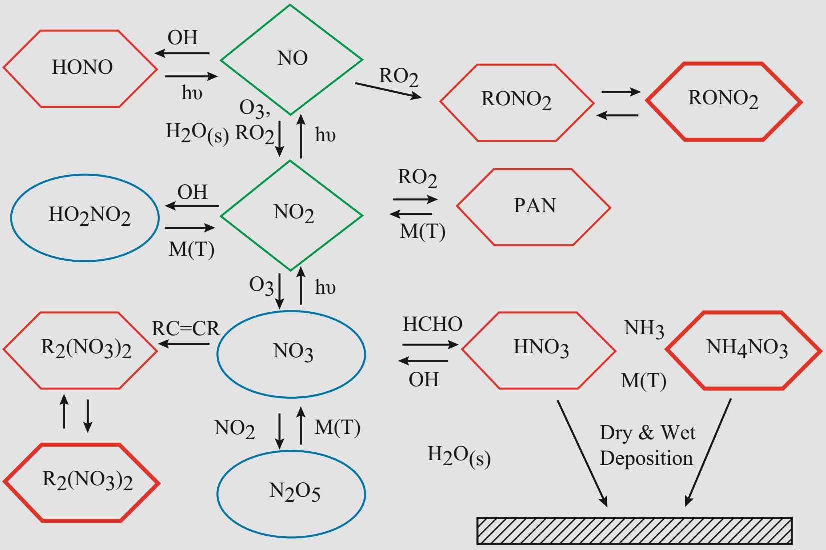

Fig. 7.7 Schematic of the atmospheric chemistry of nitrogen oxides. (Adapted from Warneck 1988)

ovals are transient species. Heavy lined hexagonal components are particle phase nitrate compounds, whose gas-aerosol phase partitioning will depend on concentration and ambient temperature.

7.4 Chemical Reactions and Influence of Space and Time Scales

The concentration and chemical transformations of air pollutants are very much affected by when and where pollutants are emitted into the atmosphere. Pollutants emitted near the ground are more likely to result in higher concentrations and exposure for local populations than those emitted from tall stacks, where point source plumes undergo substantial dispersion prior to reaching the ground. The higher the vertical placement of the emissions in the atmosphere, the greater the probability is for chemical transformation and long range transport. Transformation reactions govern chemical lifetimes of pollutants and can also affect their physical lifetimes as well (e.g., oxidized products are typically more water soluble, enhancing their dry and wet deposition).

The schematic shown in Fig. 7.8 provides an overview of emission sources, processes, and transport scales that affect regional and global air pollution. The major-

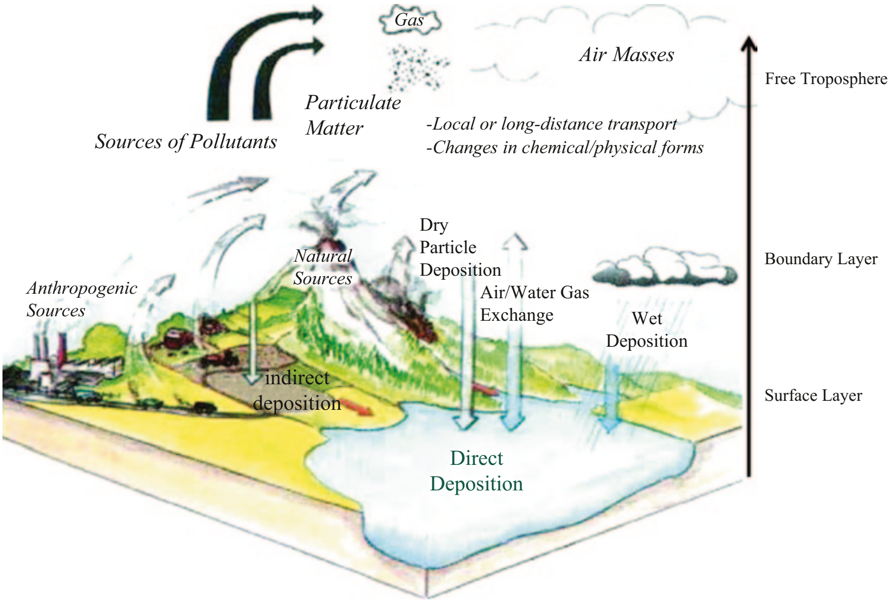

Fig. 7.8 Schematic of emission sources, processes, and transport scales affecting air pollution

ity of anthropogenic and biogenic emissions are confined to the planetary boundary layer of the atmosphere, which varies by time of day, cloud cover, season, latitude and surrounding land/water characteristics.

Ground-level sources (e.g., mobile emissions) can be confined to a night-time surface layer ranging from ten to hundreds of meters in height or to a varying daytime boundary layer, ranging from hundreds to two or three thousand meters in height, reflecting convective conditions induced by solar heating of the surface environment.

Chemical reaction rates are directly related to reactant concentrations. Local source pollutants such as automobile emissions from highways result in high concentrations on or near roadways that fall off rapidly with distance. High concentrations, over these short time periods of initial dilution, can accentuate chemical reactions that would otherwise not occur under diluted conditions. During the earliest stages of dilution (first tens of meters or so), many reactions are possible amongst the emission constituents in the exhaust as it equilibrates to ambient temperature. These can involve phase transitions, where semi-volatile organic compounds at exhaust temperature condense as they equilibrate to ambient temperature and may re-volatilize as the exhaust plume dilutes, affecting local primary and secondary organic aerosol concentrations (Robinson et al. 2007) and nanoparticle concentrations (Zhu et al. 2002). During this stage, heterogeneous reactions can form nitric acid and nitrous acid, an important photolytic OH free radical source. In addition, gas-to-particle transformations involving the transformation of sulfur to sulfate, as well as gas-phase reactions that form NO_2 and nitrosoamines. The exhaust plume entrainment stage occurs within the first 100 s and involves the mixing of the exhaust constituents by the vehicle wake and the ambient dynamics of the environment. The mixing changes equilibrium conditions within the exhaust plume and provides access to reaction channels with entrained ambient chemical species. The most important of these involve entrained ozone reactions with NO and alkenes during daytime conditions and reaction of nitrate radicals (NO_3) with VOCs during nighttime. Some of the more important reactions thought to occur during these stages of exhaust dilution are presented in Fig. 7.9.

Dispersion of pollutants in the atmosphere not only lowers concentration and exposure potential, it also slows rates of chemical reaction, extending their chemical lifetimes and consequently their transport distances. Figure 7.10 shows the temporal vs. spatial scale distribution of important chemical constituents affecting the atmospheric environment based on atmospheric lifetimes. The atmospheric lifetimes reported here may be dominated by their chemical lifetimes or their physical (wet and dry deposition or stratospheric–tropospheric exchange) lifetimes.

The highly reactive transient radical species in the first circle of Fig. 7.10 would be considered the most potentially damaging from a biochemical reactivity perspective, but their very short lifetimes might well mitigate their ability to reach critical biological endpoints susceptible to oxidative stress. Free radical chemistry is known to be extremely important in biological processes (Thannickal and

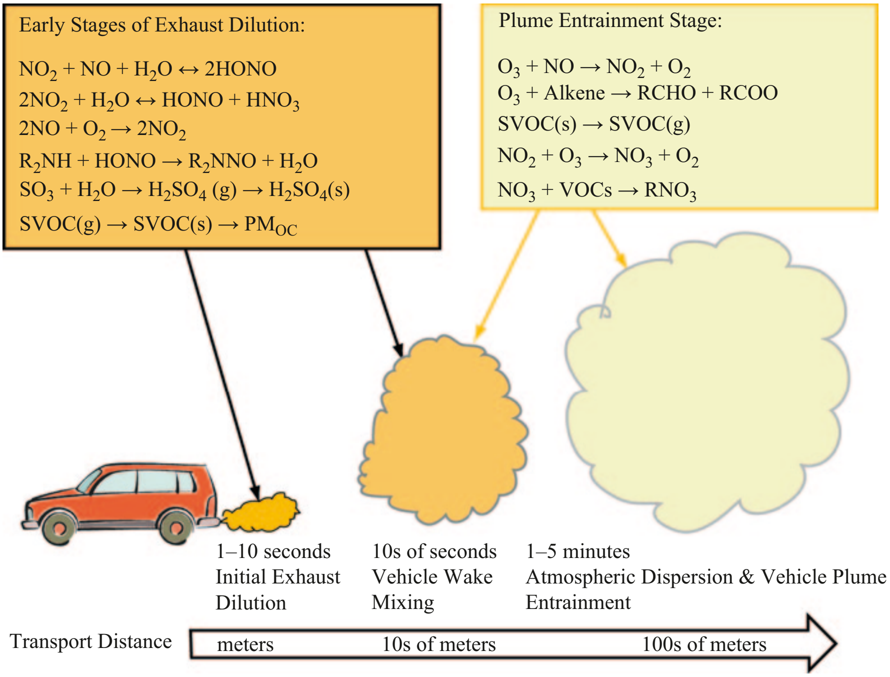

Fig. 7.9 Three stages of dilution in an idealized exhaust plume and associated potential chemical and physical transformations

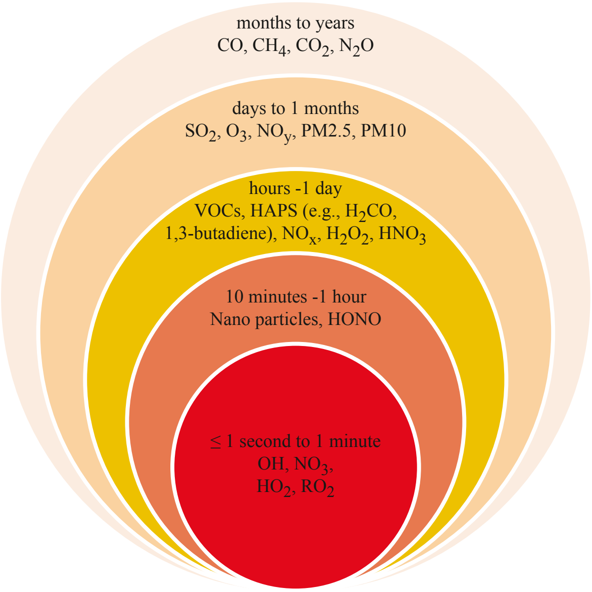

Fig. 7.10 Lifetimes and spatial and temporal scales of important atmospheric constituents

Fanburg 2000), but no direct evidence linking sources of free radical generation and health outcomes exists. Radical-generating precursor compounds generally absorb sunlight (typically <400 nm) to provide the energy necessary to break chemical bonds and produce free radicals, making sunlight a potentially important covariate. The potential health consequences and the role of free-radical-generating species (e.g., HONO, H_2CO and O_3) in the oxidative capacity of the atmosphere suggest that the free-radical generating potential of an atmospheric constituent should be a property for consideration in the development of multipollutant mitigation strategies.

7.5 The Role of Special Studies in Elucidating Atmospheric Chemistry

As previously discussed, basic understanding of the fundamental chemical reaction rates and mechanistic processes relevant to atmospheric chemistry has evolved through laboratory studies of chemical kinetics, smog chamber simulation studies, and theoretical mechanism development utilizing results from these studies. However, to fully test and evaluate our understanding of atmospheric chemistry, we must test these theoretical constructs in real world environments. Such studies improve our understanding of atmospheric chemistry and are essential in building confidence and reducing uncertainty in the chemical transformation processes simulated in air quality models. In addition, these studies uncover new chemical and physical process interactions not accessible in laboratory environments.

Special field study campaigns have played a central role in the deployment and evaluation of new measurement technologies, as well as in providing detailed characterizations of atmospheric composition. In addition they have proven invaluable in examining the effects of meteorological dynamics and the physico-chemical processes in transforming the composition of the atmosphere. These studies serve a critical need in advancing the scientific understanding necessary for informed environmental decision making. Air quality field intensive studies date back to the 1960s in the United States (Solomon et al. 2000); many examples include the Canadian Lower Fraser Valley study (Li 2004; Vingarzan et al. 2006); the EPA PM Supersites program (Solomon and Hopke 2008); the Mexico City Metropolitan Area—MCMA-2003, (Molina et al. 2007); and the Megacity Initiative: Local and Global Research Observations—MILAGRO-2006, (Molina et al. 2010). Some details of these measurement campaigns are surveyed in Appendix C (www.narsto.org) of this assessment. Text Box 7.5 highlights recent special studies performed in Canada, the United States, and Mexico and their importance in enhancing our understanding of atmospheric chemistry.

Text Box 7.5 Special Field Intensive Studies Across Canada, the United States, and Mexico

Canada

In August 2001, Canada performed a major field campaign in the Lower Fraser Valley of British Columbia. The study focused on characterizing $PM_{2.5}$ pollution in Vancouver, a major growing city in this region, which had been an intensively studied in 1993 for its ozone pollution. The four week intensive study included scientists from government, academic, and private institutions in Canada, the United States, and Europe. The study spanned measurements from a tunnel study examining motor vehicle emissions, characterizing semi-continuous (15 min) non-refractory $PM_{1.0}$ constituents through one of the first deployments of an aerosol mass spectrometer, to aircraft-based LIDAR mapping aerosol backscatter over a relatively wide area. Particle nitrate, known to be an issue in the eastern part of the Lower Fraser Valley, was studied along with biogenic sources of organic gases and particles suspected to be contributors to the pollutant burden and chemical processes in the region as a result of the dense forests in the Lower Fraser Valley and along its northern boundary.

Highlights of these studies and findings were published in special issues of Atmospheric Environment (Li 2004; Vingarzan et al. 2006). As an example, McLaren et al. (2004) studied the role of nitrate radical (NO_3) in nighttime oxidation processes and leading to the formation of inorganic and organic particle nitrate. The study involved the measurement of NO_3, total NO_y, size-fractionated particle NO_3 and particle phase organics (carbonyl compounds) on several nights. Concentrations of NO_3 of 10–50 ppt were observed overnight and N_2O_5 concentrations were estimated to be on the order of 20–200 ppt during these periods. Homogeneous and heterogeneous pathways of HNO_3 production were determined on two nights with 0.89 and 1.14 $\mu g/m^3$ of HNO_3 produced by the respective processes on night one and 1.38 and 2.56 $\mu g/m^3$ on the second night. These results suggest that a majority of the measured fine particle nitrate originated from heterogeneous N_2O_5 hydrolysis on particle surfaces. These studies also observed statistically significant nighttime increases in fine particle pinonaldehyde, believed to be due to nitrate radical oxidation of α-pinene. Results suggest that nighttime chemical transformation associated with the reaction of NO_3 radicals and biogenic VOCs are a source of biogenic organic aerosol production as well as an important link to the nitrogen cycle, which has largely been associated only with anthropogenic emissions in the Lower Fraser Valley.

United States

In 2000, the Environmental Protection Agency launched the PM Supersites Program, which was designed to address a variety of science policy based questions associated with $PM_{2.5}$ air quality issues across the country. The areas addressed included: (1) measurement methods; (2) physical and chemical characterization; (3) source apportionment; (4) atmospheric processes; and

(5) emission estimates (Solomon and Hopke 2008). Some examples of atmospheric processes investigated during special studies included: (1) the fate of nanoparticle mobile source emissions (Fine et al. 2004; Zhu et al. 2004); (2) photochemical new particle production in regional environments (Stanier et al. 2004); and (3) secondary organic aerosol production (Zhang et al. 2005a, b). In every case these findings were the result of improved measurements of time resolved aerosol composition and size (Demerjian and Mohnen 2008).

Example process science findings of interest from the EPA Supersites program include new particle formation events observed in Pittsburgh (Stanier et al. 2004) and the measurement OH and HO_2 and observational based estimates of radical sources and sinks and their contribution to the HO_x photochemical cycle in New York City (Ren et al. 2003, 2006).

The Pittsburgh studies showed that regional nucleation events were typically associated with sunny days, elevated SO_2 concentrations, and below-average $PM_{2.5}$ concentrations. Many of the events coincided with the dissipation of the stable nocturnal atmospheric layer with the onset on sunrise. Particle number concentrations peaked daily around noon, with nucleation events correlating with the product of ultraviolet intensity and SO_2 as well as showing dependence on the ambient aerosol surface available for condensation. The results suggest that the photochemical oxidation of SO_2 to H_2SO_4 plays an important role in new particle production, but that present mechanisms of binary H_2SO_4–H_2O are not able to explain the frequency or intensity of the observed events, suggesting additional sources may be contributing to the gas to particle transformations including secondary organic aerosols and chemical processes associated with ammonia.

In New York City, HO and HO_2 measurements were compared with predictions from a photochemical box model constrained by collocated precursor measurements. The summer measurements showed very good correlations between OH observation and predication during the day, but poorer correlation during the nighttime, with observations much higher than model predictions suggesting limitations in the mechanistic treatment of nighttime chemistry in the model. Hydroxyl radical levels in the winter showed similar day–night tendencies as the summer data, but with maximum concentrations levels ~1/5 of those observed in summer. OH levels are approximately an order of magnitude lower at night as compared with midday maxima and chemical mechanisms are predominantly developed and tested against smog chamber simulations of chemical systems under daytime conditions, so mechanisms have not benefited from extensive testing under no light conditions. One finding of great interest from this analysis was the significant contribution HONO photolysis in the OH budget, accounting for ~50% of the daytime OH production. The OH generated from the HONO observations suggests that there must be a significant daytime source of HONO to sustain the observed steady state concentrations during daytime conditions, when the photolytic lifetime of HONO is quite short. HO_2 correlations of observation and predictions from these studies were quite good for both day and night conditions during summer, but substantially under predicted in the winter, day and night.

These studies were among the first to directly test the radical chemistry within chemical mechanistic models under urban polluted conditions and assess the oxidation capacity of the environment. The results suggest that uncertainties remain in some of the details of the radical cycling, with better performance observed during summer daylight hours than night and greater uncertainty in HO_x chemistry in winter than in summer time conditions. Another example of the testing of radical chemistry in urban polluted environments was recently carried out in Mexico City and is discussed in the next section.

Mexico

In the spring of 2003, a major air quality field measurement campaign was carried out in the Mexico City Metropolitan Area (MCMA-2003) (Shirley et al. 2006; Volkamer et al. 2007). The campaign involved over 100 scientists from more than 30 institutions in Mexico, the United States, and Europe (Molina et al. 2007). The main goals of MCMA were to: (1) develop an improved temporal (diurnal, weekday/weekend) and spatial resolved VOC and NO_x emissions inventory for Mexico, with an emphasis on contrasting contributions from mobile versus stationary sources as well as emission sources of aldehydes, aromatics, and other organics with high ozone and secondary organic particulate formation potential; (2) develop a better understanding of the direct emission and photochemical production of formaldehyde; (3) identify major fine airborne aerosol components (sulfate, nitrate, ammonium, organics) and their contributing primary and secondary sources; and (4) characterize NO_y ambient levels and partitioning during photochemical episodes in Mexico City and better constrain the NO_y budget and identify how critical components evolve during diurnal cycles. The study provided a unique data set for an urban megacity; it has improved characterization of the complex interactions of meteorology, emissions, and atmospheric chemistry in affecting the air quality in North America's most populated and polluted megacity.

The study has provided detailed measurements of many oxidant precursors, transition products and transient species to elucidate the chemical transformation processes affecting the oxidative capacity of the Mexico City atmosphere. As in the New York City studies, measured versus predicted concentrations of OH using a constrained observational photochemical box model were in good agreement. The results show that although the OH reactivity as well as OH sources and sinks were consistently higher than most U.S. cities including levels in New York City as discussed above, the OH concentration levels were quite similar. The major observed difference in the radical pool relates to the much higher HO_2 concentrations in Mexico City as compared to other urban centers. This result is quite consistent with the high VOC reactivity and concentration levels observed in the city and the likely source of the uniquely high ozone levels, which are driven by high production levels of HO_2/RO_2. The high emission density, altitude, and unique local meteorological circulations within the MCMA present air quality challenges to the region very similar to those faced in Los Angeles, south coast air basin of CA in the late 1960s and early 1970s. It was concluded at that time that hydrocarbon emission control would be the most effective initial path to reducing photochemical oxidants. Results reported by Volkamer et al. (2007) suggest that VOC emission controls leading to reductions in VOC concentrations in the region will likely reduce concentration levels of secondary pollutants by achieving a lower VOC/NO_x ratio which effectively lowers radical re-cycling and reduces ozone production efficiency and slows the formation of secondary pollutants.

7.6 Rationale for a Multipollutant Strategy: An Atmospheric Chemistry Perspective

As has been shown in the preceding discussions, atmospheric chemistry provides many common threads to multipollutant air quality outcomes of interest to this assessment. The photochemical oxidation of atmospheric chemical constituents and their physical removal by wet and dry deposition are the major cleansing mechanisms in the atmosphere. The atmospheric lifetimes of chemical constituents emitted and transformed into intermediate and terminal products play an important role in defining multipollutant air quality environments and their potential hazard to human health. The formation of secondary organic aerosols typically involves the partial oxidation of VOCs incorporating oxygen and nitrogen (possibly sulfur as well) in the form of carbonyls, peroxides, acids, nitrates, nitrites, amines and organo-sulfur compounds. It is likely that pollutant mixes are more toxic than any one of the individual components in those mixtures, but quantifying multipollutant health effects remains an unresolved challenge.

Our knowledge of atmospheric chemistry can provide possible insights as to what combinations of chemical and physical properties and environmental conditions are most likely to result in toxicity and associated health impacts. A possible approach would be to characterize the potential toxicity of multipollutant mixtures based on the intersection of their key chemical and physical properties and the exposure environment in which they are most likely to be found. For example, does regional ozone mixed with fresh urban emissions have a higher or lower toxicity or health response than an aged regional ozone environment that is unperturbed? Conceptually, differences in weekday and weekend smog conditions are a case in point. Weekday ozone concentrations develop in urban centers as a result of regional ozone entrainment/transport and/or photochemical formation in the presence of high local emissions. In contrast, weekends in many instances have similar ozone

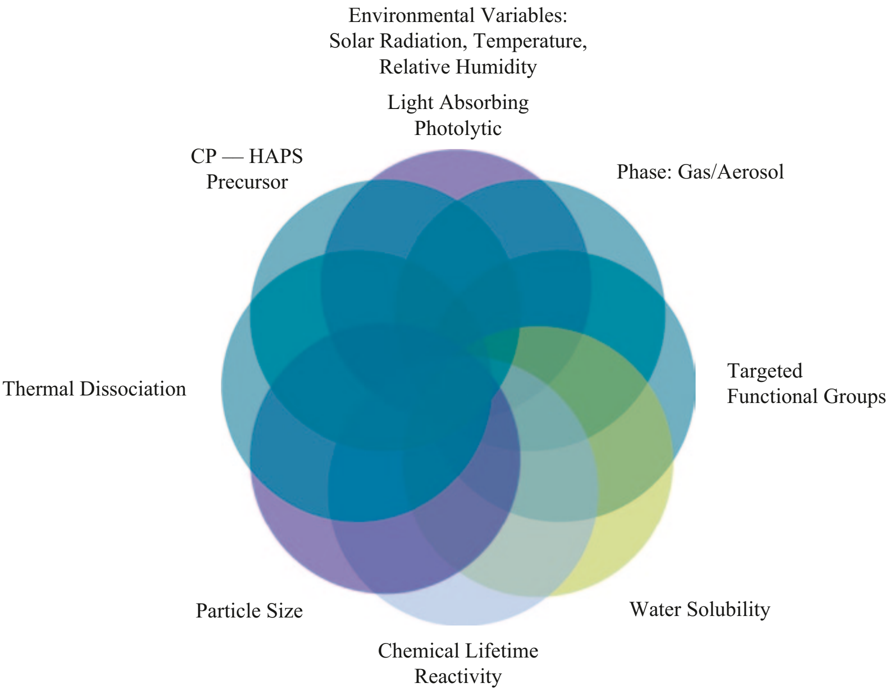

Fig. 7.11 Characterization of the potential toxicity of multipollutant mixtures by their chemical and physical properties and environmental conditions

concentration levels as weekdays (likely due to ozone entrainment/transport) but with a significant reduction in local fresh emissions and different associated precursor conditions. Such contrasting environments may show distinct differences in health outcomes for comparable incremental changes in ozone. The chemical characterization of these contrasting multipollutant environments would provide insight as to the chemical properties and interactions most likely affecting the observed ozone health response relationship. A broad conceptual view of how multipollutant mixtures may interact to affect their potential toxicity is illustrated in Fig. 7.11.

7.7 Conclusions and Current Outlook

Improvements in chemical mechanisms come as model application demands are induced by pending regulatory deadlines (e.g., the NO_x SIP Call; see also Chap. 12). Unfortunately the research and development lead time to further develop process modules and models is always too short and the resources are always too limited. Recent model evaluation studies of $PM_{2.5}$ predictions indicate substantial overprediction in $PM_{2.5}$ mass and significant underprediction of the organic fraction of

$PM_{2.5}$ (Hogrefe et al. 2009). The discrepancies are likely related to emission and chemistry information, with the treatment of the production of secondary organic aerosol and its partitioning in the volatile, semi-volatile and liquid/solid aerosol phases a major factor requiring further development.

Demonstrating accountability in the management of ozone air quality remains untested as a result of limited observational data from measurement networks for tracking changes in precursor concentrations over extended periods of time. Accountability in the management of $PM_{2.5}$ air quality poses potentially even greater challenges should one or more PM components or particle number become better targets in affecting health outcomes.

Recent emission changes resulting from the introduction of ultra-low-sulfur diesel fuel may be detectable via special field intensives in the short term and effects of the introduction of the 2007 heavy duty diesel engine standard may be observable in the longer term (depending on fleet penetration and the robustness of diesel emission control technology, e.g., particle filter traps).

Current monitoring networks routinely measure a few dozen chemical constituents in the atmosphere. The compounds monitored are generally associated with criteria pollutants and their precursors. The monitoring of air quality outcomes in response to future multipollutant emission control strategies poses a challenge for current monitoring resources and raises the recognized fundamental need for special study field measurement capabilities within national monitoring networks.

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Chapter 8
Source Emissions in Multipollutant Air Quality Management

C. Andrew Miller

The purpose of this chapter is to discuss the current understanding of source emissions in a multipollutant air quality management context and to recommend steps that are needed to improve the ability of source-related measurements to support risk- and results-based multipollutant air quality management. As noted earlier, this approach is seen as providing a substantial opportunity for improving the desired reductions in adverse health and environmental effects at the same or lower cost than is now the case. Emission inventories, and the measurements and methods associated with the development of these inventories, were discussed in detail in the NARSTO (2005) Emission Inventory Assessment (EIA); the EIA provides a foundation for the current discussion. In a multipollutant/accountability framework, however, components of emission measurements and estimates warrant discussion beyond that in the EIA.

Although air quality management is usually concerned with the amount of pollutants in the atmosphere, the strategies developed and implemented to achieve improved air quality require management of source emissions. These strategies involve either reducing the magnitude of the underlying activities that produce pollutant emissions or removing pollutants from the processes involved in these activities. The latter approach is achieved through the use of control technologies, process design changes, or changes in fuels and other process inputs. Other risk management approaches are used to reduce exposure to the resulting pollutants by isolating emission-producing activities from populations or other receptors. Such exposure reduction approaches (such as warnings aimed to encourage susceptible populations to remain indoors) are usually tied to predictions of poor air quality during specific meteorological and emission conditions. In general, North American air quality management strategies have focused on achieving ambient air quality goals through emission reductions, which in many cases are the foremost measure by which the success of air quality management strategies are determined. Air quality managers have reserved exposure reduction approaches to situations in which

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emission reduction strategies have not been successful in reaching target air quality levels.

A multipollutant view of sources means more than simply measuring or controlling the different types of pollutants that may be emitted from a single source. It also implies effective management of the different sources that, in combination, emit the multiple pollutants and pollutant precursors within an airshed. In practice, many of the major regulatory actions in North America have been effectively multipollutant in character within *Levels 1* and *2* as described in Chap. 3. Approaches to reducing ozone and particulate matter (PM), for instance, require management of a range of precursors (e.g., NO_x and VOCs) that are emitted from different source types (see also Chap. 12).

From an accountability perspective, emission measurements and estimates need to be of sufficient quality to provide stakeholders with information that will demonstrate whether the anticipated changes in emissions associated with air quality management strategies are occurring in practice. To meet this need, emission measurements and estimates must be of sufficient accuracy, precision, scope, and detail to evaluate changes in emission amount, composition, time, location, and ultimately, effects (see Figs. 3.1 and 3.2). Emission inventories are the primary means by which measurement and estimation data are collected and reported.

8.1 Emission Inventories in Current Practice

Two source-related issues are crucial to the design of successful air quality management strategies at *Levels 1*, *2* and beyond: (a) whether the emissions from the range of sources within a given air quality management area are known with enough accuracy to enable air quality managers to develop projected emission reduction strategies; and (b) whether the emission reduction strategies provide the anticipated reduction in emissions and the subsequent reduction in ambient pollutant concentrations. The first issue was discussed in detail in the EIA (NARSTO 2005), although in the context of the single-pollutant air quality management strategies that typify current North American practice. Because of the importance of emission inventories in air quality management, we will briefly discuss the EIA recommendations and extend the discussion to address some of the differences between a multipollutant approach and the current single pollutant approach.

The EIA described in detail many of the challenges facing analysts developing emission inventories, and it offered a number of recommendations for addressing those challenges. In general, the EIA concluded that current emission inventories are in need of considerable improvement to provide the range and quality of traceable information that air quality managers require to develop effective air quality management strategies.

The EIA presented eight principal recommendations, listed in Text Box 8.1, for improving emission inventories across North America. These recommendations continue to be important drivers not only for single pollutant considerations, but also for multipollutant management. In the following paragraphs, we focus on the findings of the EIA that are particularly applicable to a multipollutant/accountability approach to air quality management.

Text Box 8.1 NARSTO (2005) Emission Inventory Assessment Recommendations

1. Reduce Uncertainties Associated with Emissions from Key Under-characterized Sources
2. Improve Speciation Estimates
3. Improve Existing and Develop New Emission Inventory Tools
4. Quantify and Report Uncertainty
5. Increase Inventory Compatibility and Comparability
6. Improve User Accessibility
7. Improve Timeliness
8. Assess and Improve Emission Projections

EIA recommendations 3 (Improve Existing and Develop New Emission Inventory Tools) and 8 (Assess and Improve Emission Projections) have implications for inventory methods development, for projecting future emissions, and for documenting and understanding changes in emission trends over time. Maintaining long-term traceability of methods used to estimate emission trends is often in conflict with the understandable desire to make continual improvements in those methods. These improvements are driven by strong technical and regulatory interests in improving the accuracy and completeness of contemporary emission data. Improved methods can incorporate updated relationships between pollutants (e.g., evaluation of mobile source models[1]), new definitions of pollutants (e.g., condensable PM), reduced measurement artifacts and biases, or other changes that differ substantially from previous techniques. Thus, comparability with previous inventories is often not possible. Of the two key components needed to evaluate long-term emission trends (baseline data and trend integrity), inventories typically generate current baseline data, but often lose trend integrity by redefining a baseline arbitrarily as inventory methods are improved. Those responsible for developing updated or new measurement methods, inventories, or databases need to intentionally plan for and implement the means for enabling long-term emission data comparability as new updates are developed and implemented (backward compatibility in computer software terms). The EIA called for changes in measurement methods, emission models, and speciation profiles to improve the accuracy of emission inventories, but these changes need to be incorporated into existing inventories such that it would remain possible to compare results over time to enable meaningful evaluations of long-term emission changes.

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[1] EPA's current mobile source models are MOBILE6 for on-road vehicles and NONROAD for non-road engines, equipment, and vehicles. EPA's Office of Transportation and Air Quality (OTAQ) is currently developing a new modeling system termed the Motor Vehicle Emission Simulator (MOVES).

In a multipollutant approach, the need for robust data that can link sources to ambient concentrations also means that the data sources used to develop inventories need to be consistent with one another. The EIA pointed out that current inventories are often based on very different collections of basic information, particularly for other than criteria pollutants (CPs). These inconsistencies in data sources were the focus of Recommendation 5 (Increase Inventory Compatibility and Comparability). EPA's updated Emission Inventory System Implementation Plan has addressed the issue of data sources, and is intended to reduce these inconsistencies (EPA 2008).

For the balance of this section, we focus on the second issue (whether the emission reduction strategies provide the anticipated reduction in emissions and the subsequent reduction in ambient pollutant concentrations) by discussing approaches for evaluating the accountability of air quality management strategies. In the discussion, we examine the goals and impacts of a few major programs to determine whether they have achieved the desired reductions in emissions. The strategies that emerged from those programs have resulted in major changes in the development and use of pollution control technologies, including changes in the emitting processes, composition of the fuels used in those processes, and flue gas or tail-pipe treatment systems. These changes have been driven by regulatory requirements, most of which addressed emission reductions at a national level, with additional intervention at the provincial, state, and local levels. The national commitments allow the pollutants' impacts to be evaluated on a scale large enough to minimize significant local variability from meteorological factors and demography that may mask the larger-scale trends.

While the first level of accountability related to emission reduction programs is the measured or estimated change in emissions, the second level of emission accountability is the analysis of the changes in measured ambient concentrations of the pollutant(s) of interest. Issues associated with these measurements are discussed in detail in Chaps. 10 and 12, but are noted here in the context of emission changes. EIA recommendation 4 (Quantify and Report Uncertainty) addressed the need for using top-down approaches for the evaluation of accuracy of emission inventories based on ambient data and source-receptor modeling.[2] In many cases, the methods used for ambient monitoring may be more consistent over time than the methods developed for emission inventories and models. Thus the ambient data provide an indirect means to evaluate expected long-term trends as emission reduction strategies are implemented (e.g., Chap. 12). However, for some emission reduction programs, long-term ambient data are not sufficient to provide a complete evaluation of the success of those programs. In the case of hazardous air pollutants (HAPs), for example, the existing monitoring networks do not adequately cover multi-city conditions with the relatively small spatial domains and long temporal scales that are of

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[2] Top-down tests of emission inventories are tests conducted outside the structure of the emission inventory. They do not explicitly consider the individual components (e.g., emission factors or activity factors) that go into the development of inventories from the bottom up. Rather they consider independent information such as ambient measurements of the emitted species. Taken from the EIA [Chap. 8: Top-Down Assessments of Emission Inventories (NARSTO 2005)].

greatest concerns for these pollutants, many of which are classified as carcinogens. In some cases, the monitoring methods are not designed to provide data on HAPs of interest, further limiting the ability of monitoring to provide a means to evaluate actual changes in ambient concentrations due to emission reductions (e.g., Chap. 10).

The use of source-receptor modeling requires that the source-emission composition profiles be robust enough to support broad application of this approach as a means to link ambient measurements to source types in widely different locations. This method requires that source-emission profiles be up-to-date and collected from a representative sample of sources within each source category to reflect the range of emission composition and activity patterns. Improved source emission profiles were identified as a key need in the EIA, which specifically recommended the development of improved and new source profile data. EPA's SPECIATE database provides speciation profiles of emissions from air pollution sources for total organic compounds and both inorganic and organic species in PM. The database is in its fourth major revision, released in December 2006 (EPA 2006). Data submitted to the EPA inventory process focus on state, local, and tribal agencies and regulated sources, and speciated profiles are not part of the required submission. Similar practices exist in Canada and Mexico; allowing proactive submission of third party speciation data (submitted by other than agencies or regulated sources e.g., http://www.cec.org/naatlas/prtr/) that can provide an additional means of improving speciation profiles.

Particularly for mobile source and air toxics programs, the application of ground-based remote sensing technologies can provide a means to directly evaluate emissions from roadways or industrial facilities (as opposed to measuring emissions from single vehicles or point sources that are assumed to be representative of similar sources in their class). Remote sensing can also provide data from in-use vehicles that can yield emission measurements as a function of fuel consumption rather than emission factors that are related to engine energy output. These measurements can be used in conjunction with emission inventory estimates derived from fuel consumption data, providing a (partial) accountability measure for inventories based on vehicle miles traveled and fleet characteristics. Both remote sensing and fuel-based inventories are discussed in detail in the EIA (NARSTO 2005).

The EIA provided a summary of the strengths and weaknesses of emission inventories in general; this discussion will not repeat those details. Nevertheless, the needs for reliability and estimates of uncertainties identified for inventories in general are at least as important in a multipollutant air quality management context as they are for existing air quality management approaches.

The EIA recommendations are directly applicable to multipollutant air quality management because, to a large extent, many of the recent major regulatory actions in the United States, Canada, and Mexico have been of multipollutant character in addressing emission reductions, even if they are based on a single pollutant regulatory structure. In Canada, management of ozone has involved not only local VOC and NO_x precursor considerations, but also concern for long-range transport of oxidant mixtures across the U.S.-Canada border (see also Chap. 12). In Mexico, the management of ozone concentration levels has involved evaluation of the consequences of changing VOC and NO_x emissions in concert both in Mexico City and in other urban locations (see also NARSTO 2000; McMurry et al. 2004). The development of emission inventories for air quality management in Mexico is summarized in Text Box 8.2. Additional detail for Mexico is included in Appendix B (www.narsto.org).

Text Box 8.2 Development of Emission Inventories in Mexico

Emission inventories for various pollutants in Mexico have been developed through SEMARNAT, the Mexican federal environmental agency, mainly for major urban areas (e.g., Mexico City and several cities along the Mexico-U.S. border) with particular emphasis on large point sources. The first national emissions inventory (MNEI), which includes criteria pollutants and precursors, was produced for the year 1999, and was released in September 2006 (SEMARNAT 2006a). This inventory was developed in partnership with EPA, the Western Governors Association (WGA) and the North American Commission for Environmental Cooperation (CEC). The development of the MNEI follows similar techniques used by Canada and the United States, through the use of emission factors, emission controls and activity patterns applicable to Mexican sources, including a special version of MOBILE6 and the use of EPA's AP-42 guidance. The MNEI for the year 2005 will be released in 2011. Biogenic emission inventories that include non-methane VOCs from vegetation and NO_x at the national level have been developed (SEMARNAT 2004). Greenhouse gas emissions are also being estimated at the national level from 1990 to 2002 for CO_2, CH_4, N_2O, HFCs, PFC, and SF_6. The latest report was published in 2006 (SEMARNAT 2006b). Large databases, such as the Registry of Pollutant Release and Transfer (RETC), compile emissions data at the national level in a single data depository. The RETC contains data of 104 substances reported by industries under federal jurisdiction; it is being gradually implemented by local authorities to collect information under state and municipal jurisdictions. The RETC database is available at http://app1.semarnat.gob.mx/retc/index.php.

In addition to the MNEI, a number of emission inventories for urban areas in Mexico have been developed by different government entities addressing various objectives. Specialized inventories for multipollutant sources have been developed for Mexico City, Monterrey, Guadalajara, Toluca, Mexicali, Tijuana, Ciudad Juarez, and other urban areas (see Appendix B). However, there are important differences between these inventories such as the base year of the emissions, the number and type of source categories included, and data quality and validation protocols. The most detailed emission inventory is that of the metropolitan area of Mexico City, which has been under continuous biennial development since 1994 [Comision Ambiental Metropolitana (CAM) 2006] and includes annual emission estimates for CO, NO_x, SO_2, VOCs, MHC, NH_3, PM_{10} and $PM_{2.5}$. A toxic emission inventory for Mexico

City, which has been under continuous biennial development since 2004, contains annual emissions information for 109 compounds from point, area, and mobile sources for the Mexico City Metropolitan Area. The latest emission inventory is for the year 2006 [Gobierno del Distrito Federal (GDF) 2007].

Because of strong concern for high levels of ozone and particulate matter, measurements and modeling activities have focused on speciated VOCs and NO_x emissions, as well PM_{10} or $PM_{2.5}$ mass concentration and bulk composition (see also Appendix B). While some measurements of emissions from stationary sources (e.g., Mejía et al. 2007), area sources (Velasco et al. 2005a, b) and biogenic VOC (Domínguez-Taylor et al. 2007), have been reported recently, much of the effort has been concerned with motor vehicle emissions, particularly in Mexico City. Investigations have ranged from vehicle dynamometer studies (e.g., Jazcilevich et al. 2007) to remote sensing (Schifter et al. 2003) and mobile laboratory sampling (Zavala et al. 2006, 2009a).

The validation of the emission inventory estimates for Mexico City has been performed through techniques including inverse air quality modeling and source apportionment approaches (Vega et al. 1997, 2000) and direct emission measurements (Schifter et al. 2003; Velasco et al. 2005a, b; Zavala et al. 2006, 2009a). Acquisition of knowledge about the emission characteristics of sources, especially in Mexico City, has substantially improved the ability to conduct air quality analysis in support of policy-making in Mexico (see also Appendix B).

8.2 Multipollutant Emissions

The source categories that account for the largest mass of emissions are typically emitters of multiple pollutants. In terms of total mass emissions, the largest sources of air pollution by mass generally are combustion processes, including electric power generation, transportation, industrial processes, and largely uncontrolled biomass combustion (EPA 2003). High temperature combustion processes are fundamentally chemical reactions that generate, via incomplete combustion, products such as carbon, CO, volatile and semivolatile organic compounds (VOCs and SVOCs)—some of which are listed as HAPs (see the List of Terms), and carbonaceous particles. They often use fuels that emit significant amounts of impurities such as sulfur and metals after combustion. Fuel combustion, therefore, is an inherently multipollutant emission process.[3]

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[3] Large intermittent (fugitive) sources also are important by mass emissions, including wildfires and blowing soil dust (e.g., McMurry et al. 2004; NARSTO 2005). These sources require management in a distinctly different way compared with stationary or transportation sources.

Table 8.1 Example integration of pollutants by generic source. (The shading denotes emissions of the pollutants by the indicated sources: see text)

	Gaseous Fuel Combustion	Liquid Fuel Combustion	Solid Fuel Combustion	Metal processing—smelting and steel production	Petro-refining and petrochemical processes	Halogen – organics and pesticides manufacture	Amino and other nitrogenous compounds from manufacturing
Carbon oxides (CO, CO_2)	░	░	░	▓	(c)	(c)	(c)
Nitrogen oxides	░	░	░	▓	(c)	(c)	(c)
Sulfur oxides	░	░	░	▓	(c)	(c)	(c)
(generic) Volatile organic compounds	░	░	░		▓	▓	▓
(generic) Particulate matter including carbon compounds	░	░	░	▓	▓		▓
Aldehydes		░	░		▓		
Benzene, toluene, ethylene, xylenes (BTEX)		░	░		▓	▓	▓
Other (non-sulfur) acid gases		░	░	▓	▓	▓	
Mercury compounds			░	▓			
Other metals and metal compounds		░ (a)	░	▓	▓ (catalysts)		
PAHs		░	░		▓		
Halogenated organic compounds			(b)			▓	
Vinyl Compounds					▓		
Amines and other nitrogenated organic compounds							▓
Other sulfur compounds						▓	
Phthalic and maleic compounds						▓	

(a) Metal emissions primarily from heavy fuel oil combustion. Trace quantities of metals may be in vehicle exhaust due to engine component wear.

(b) Halogenated organic emissions primarily from waste combustion processes.

(c) Fuel combustion emissions can also occur from chemical processing facilities, but are considered to be under the fuel combustion headings in this table.

In the United States, the inherently multipollutant character of emissions from key source categories is illustrated in Table 8.1. The grouping of sources for different pollutants is similar in Canada and Mexico. Mobile sources, utilities, and industrial fuel combustion processes emitted 10% or more of the total U.S. national emissions in 2003 for two or more CPs, and emitted measurable quantities of all of the inventoried CPs (except lead) and precursors of secondary pollutants (CO, NO_x, PM_x, SO_2, VOCs and NH_3). In this table, PM includes a condensable fraction, and it also includes total $PM_{2.5}$ emissions. With the exception of a "solvent utilization" category (chemical processing or halocarbon organics), the remaining top-tier source categories all emit measurable amounts by mass of four or more of these pollutants.

Many of the general source categories include a diverse range of emission points within an industrial cluster that are not necessarily multipollutant in character. In some cases a "miscellaneous" category is listed in inventories, which usually includes mass emissions otherwise unaccounted for. In a given facility, different pollutants can be emitted from very different and independent processes, such as ammonia from agricultural applications and livestock operations and fugitive dust (usually PM_{10}) from agricultural operations, or from unpaved roads. These sources contrast with the chemical manufacturing and petroleum industry categories, which may emit multiple pollutants from many processes occupying the same site. Both of these industrial source categories typically include a diverse range of emission processes within a single facility, including fugitive, speciated VOC or other emissions from leaks and vents, or emissions from combustion processes in heaters and flaring of waste gases. Because the different processes occurring within an industrial facility are often interconnected, they are not completely independent of one another, and they are not as suitable to multipollutant control technology options as are sources such as motor vehicles or boilers in fossil-fueled power plants and industrial facilities.

Table 8.1 provides an illustration of the relationships between broadly defined source types and the different classes of pollutants. The portions of the table that are lightly shaded indicate that these pollutants are emitted as a mixture with the other classes of pollutants from a single point effluent. Those portions of the table that are shaded darker indicate that the pollutants from those sources are mostly emitted from effluent points that are distinct from one another, even though they may be emitted from a single facility. The unshaded areas indicate that those source types do not typically emit those particular pollutants. For example, the light shading under Solid Fuel Combustion indicates that all the pollutant classes from carbon oxides to polycyclic aromatic hydrocarbons (PAHs) are emitted from a single exhaust point—they are present in the untreated flue gases from coal combustion, for instance. In contrast, a range of different VOCs and HAPs may be emitted from petroleum refineries or petrochemical units across a plant site, but they are usually emitted separately from distinct emission points, such as process leaks, valves and pump seal leaks. Finally, one does not expect to see emissions of metals in the exhaust of gaseous fuel combustion, given the lack of metals (except perhaps very low levels of mercury) in a refined fuel. However, very often combustion emission processes are correlated with metal emissions, because the combustion processes are often associated with degassing and eroding metallic components in engines or process equipment.

The grouping in Table 8.1 could be used as a means of classifying multipollutant emissions by source, which could assist in developing a plan for optimizing multipollutant emission controls by common source. In Chap. 7, we introduced the potential for grouping by chemical properties or by reactivity. A hypothetical example is given in Fig. 7.11. In principle, grouping also could be done by health or ecological effects (e.g., Chap. 5), but specifics of this approach are excluded from this study due to our limited current state of knowledge regarding relevant toxicological effects.

When a range of pollutants is considered, the multipollutant nature of many, if not most, source types becomes even more complex. Traces of HAPs and greenhouse gases, for instance, are (for practical purposes) present in all combustion emissions. The compounds present in carbonaceous PM typically contain some level of toxic organic HAPs, such as PAHs. The inclusion of these pollutants can modify the relative importance of source categories in the development of air quality management strategies. As an example, municipal waste incinerators are a minor contributor to CPs on a national scale, but were a major source of mercury emissions in the United States prior to the 1990s. Likewise, consideration of methane (CH_4) in the context of greenhouse gas emissions can make sources such as pipeline and storage tank leakage, solid waste landfills and other waste treatment facilities, and feedlots more important than they would be if only VOCs were considered. Even when evaluating control strategies for CPs alone, the impacts on more broadly defined air quality criteria, including climate issues, can change the overall effectiveness of a control strategy. For instance, reducing NO_x as an ozone control can lead to long-term regional increases in methane from the NO_x–CH_4–ozone chemistry in the atmosphere, potentially resulting in a net increase in warming (Wild et al. 2001). Thus, not only are multiple emissions important to characterize in a multipollutant context, but the impacts on atmospheric chemistry due to those emissions need to be accounted for as well (see also Chaps. 7 and 11).

In summary, the major sources of air pollutant emissions are largely multipollutant in character. Although the enormous strides made in reducing North American air pollutant emissions over the past four decades have been based on today's single pollutant regulatory framework, the implementation of these regulations in practice has a multipollutant character. This characteristic is particularly true for regulations designed to reduce precursors of ambient ozone including emissions from mobile sources.

8.3 Multipollutant Control Strategies

To better understand how multipollutant control strategies can be structured and how the performance of those strategies can be evaluated, it is fruitful to examine selected past and current regulatory programs. For illustration, Table 8.2 provides an overview of some of the key air pollution reduction programs over the past three decades, including the expected emission reductions and actual reductions achieved. The listing includes initiatives for stationary sources including electricity generating units, transportation sources, and industrial or commercial processing. These programs, either complete or in progress, represent major public commitments to reduce a broad range of CP and HAP emissions to improve air quality. Much attention has been given to ozone and to its precursors, as well as sulfur and nitrogen emissions for other purposes, including particulate matter and acid deposi-

Table 8.2 Examples of major initiatives for emission reductions in North America intended to improve air quality. (These programs offer opportunities for accountability analyses)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (Actual reductions underlined)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
U.S. power plant sources					
Acid Rain Program—CAAA Title IV	1996: Phase 1 2000: Phase 2	Certain coal-fired EGUs (boilers only) subject to Title IV in eastern and midwestern states; for SO_2, Phase 1 affected 263 units (became 445 units) and Phase 2 affected 2000+ units; for NO_x, Phase 1 affected ~170 boilers and Phase 2 affected certain boilers in addition to the 170	Goal: 10 million t reduction in SO_2 from 1980 levels, 2 million t reduction in NO_x In 2005 Progress Report: SO_2 emissions reduced by over 5.5 million t from 1990 levels, or about 35% reduction, for power sector; 7+ million t (41%) less than 1980 levels; NO_x emissions reduced by ~3 million t from 1990 levels (~50 reduction)	Comparison of CEM measurements with eastern regional scale NO_x, NO_y and SO_2; particle SO_4 and NO_3; ozone—especially east of the Mississippi River and southeastern Canada. Comparison with dry and wet deposition and water chemistry in vulnerable surface waters. Track aquatic and terrestrial ecosystem biota and soil conditions in acid vulnerable areas. (n.b. studies already in place and have demonstrated tracable changes except for biota.)	http://www.epa.gov/airmarkets/progsregs/arp/index.html
NO_x SIP Call	2004–2007, depending on state	EGUs large industrial boilers, and turbines in 20 eastern states and D.C.	NO_x cap of 506,000 t (2003 goal); 491,000 t actual (2006)	Comparison with CEMs for NO_x emissions; regional scale and urban measurements of NO_x, NO_y, ozone, particle NO_3; special studies of odd nitrogen balance, including PAN and other trace N species. Design and deployment of special studies for public health improvement—no known plans. (n.b. Air quality measurements in place and comparison with modeling undertaken; effects tracking principally in acid deposition context)	http://www.epa.gov/airmarkets/progsregs/nox/sip.html

Table 8.2 (continued)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (Actual reductions underlined)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
Clean Air Interstate Rule (CAIR)[a]	2009: Phase 1 NO_x 2010: Phase 1 SO_2 2015: Phase 2, full implementation	Fossil-fuel fired EGUs in 28 eastern states and D.C. (3 states: NO_x ozone season only; 3 states; NO_x annual only; 22 states and D.C.: both NO_x ozone season and annual)	Projected NO_x reductions of 2 million t/year by 2015 (61% reduction from 2003 levels) Projected SO_2 reductions of 7 million t/year by 2015 (73% reduction from 2003 levels)	CEMs measurements for SO_2 and NO_x emissions; regional and urban (eastern US and southeastern Canada) measurements of SO_2, NO_x, NO_y, and ozone; particle SO_4 and NO_3; acid deposition in vulnerable areas; measurements of surface water chemistry and aquatic-terrestrial biota/soils. Special measurements for N balance. Design for special studies to examine regional vs. urban contributions of PM and ozone Design for special public health studies in major urban examples—perhaps NE cities and Toronto area. (no known plans for health studies; reliance on principal monitoring networks, without special studies.)	http://www.epa.gov/interstateairquality/basic.html http://www.epa.gov/airmarkets/progsregs/cair/index.html
U.S. mobile sources					
Tier 2 Vehicle and Gasoline Sulfur Program	2004: Gasoline sulfur content 2004–2009: Phase-in of new vehicle standards by model year (MY)	Gasoline sold nationwide; cars, light-duty trucks, and certain size SUVs sold outside CA	NO_x reductions of 2.8 million t/year by 2030. Also reduces VOCs	Provide traceability to dynamometer vehicle testing, and implement on road vehicle surveillance for changes in sulfur and nitrogen emissions and perhaps speciated VOC emissions (note effects of fleet changes or catalyst deterioration). Connect ambient monitoring for NO_x, ozone, PM with intermittent (but scheduled long term) roadside studies for tracking	http://www.epa.gov/otaq/regs/ld-hwy/tier-2/index.htm

Table 8.2 (continued)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (Actual reductions underlined)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
				NO_x, SO_2, PM and speciated VOC concentrations. Seek opportunities for specialized health related studies linked with expected change in motor vehicle emissions (no known designs for this change)	
Heavy Duty Highway Diesel Program	2006: Diesel sulfur content 2007 (MY): Begin phase-in of new engine standards	Diesel fuel sold nationwide; heavy-duty highway diesel engines (trucks, buses, etc.) nationwide	NO_x reductions of 2.6 million t/year by 2030; also reduces VOCs	Same as for gasoline sulfur initiative; added emphasis on diesel emission changes and link with potential health effects	http://www.epa.gov/otaq/highway-diesel/index.htm
Clean Air Non-road Diesel Program	2007: Diesel sulfur content 2008 (MY): begin phase-in of new engine standards	Non-road diesel fuel sold nationwide; diesel engines nationwide used in most construction, agricultural, and industrial equipment	NO_x reductions of 738,000 t/year by 2030; also reduces VOCs	Urban monitoring surveillance for SO_2 and other diesel related species; design of special source based studies of nonroad diesel engines including heavy duty construction equipment, railroad locomotives for changes in NO_x, speciated VOC and sulfur emissions with fuel composition changes. Design for source oriented health based study workers and neighborhoods potentially exposed to sustained emissions (e.g. rail yards)	http://www.epa.gov/nonroad-diesel/2004fr.htm

Table 8.2 (continued)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (<u>Actual reductions underlined</u>)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
Hazardous air pollutants from mobile sources (MSAT 2)	2009: VOC controls on gas cans 2010 (MY): Begin phase-in of new engine standards 2011: Gasoline benzene content	Gasoline-fueled passenger vehicles nationwide; gas cans nationwide; gasoline sold nationwide	VOCs reductions >1 million t/year by 2030	Design for accounting for vehicle emission testing, including dynamometer tests, and on-road vehicle tracking. Design for specialized sampling of HAPs related evaporative and exhaust emissions (including aromatics, acrolein, 1,3-butadiene, formaldehyde and acetaldehyde). Designs for roadside or traffic related studies with intermittent, but regularly scheduled, repeated studies as vehicle fleet changes. Studies to account for changing fuel composition seasonally and in the long term. Special studies for identification of VOCs not designated as HAPs but potential health factors (e.g., organonitrates). Design for health related near roadway studies and toxicological exposure investigations related to non-designated HAPs	http://www.epa.gov/OMS/toxics.htm

Table 8.2 (continued)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (Actual reductions underlined)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
Canadian mobile sources					
Sulfur in Diesel fuel regulations	2006: On-road diesel sulfur content 2007–2008: Off-road diesel fuel content	Diesel-fueled on-road vehicles, off-road vehicles and rail and marine engines	SO_x, NO_x, VOCs and PM emissions from new heavy-duty diesel engines reduced by about 90, 90, 89, and 90% respectively	Same as for U.S. gasoline sulfur initiative; added emphasis on diesel emission changes and link with potential health effects	http://www.ec.gc.ca/ceparegistry/documents/regulations/qa_guid/questions.cfm
Mexican mobile sources					
Specifications for Low Sulfur (LS) fuels for on-road vehicles	Phase in by January 2007 in northern border region; January 2009: three metropolitan areas (Guadalajara, Monterrey, and Valle de México); September 2009: nationwide	Light and heavy duty vehicles	Projected sulfur reductions 73–92% in gasoline (to 30 ppm sulfur avg.) and 92–97% in diesel fuel (to 15 ppm sulfur). Direct reductions in SO_2 and PM emissions; phase in control technology for new vehicles	Same as for U.S. gasoline sulfur initiative; added emphasis on diesel emission changes and link with potential health effects	http://www.ordenjuridico.gob.mx/Federal/PE/APF/APC/SEMARNAT/Nomas/Oficiales/2006/30012006(1).pdf

Table 8.2 (continued)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (Actual reductions underlined)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
Phase in control technologies for vehicles	LDV-2004–2009 models: emiss. equiv. to US Tier 1 std. 2007–2010 models: Tier 2 Bin 10 std. >2010 models: Tier 2 Bin 7 std	LDV gasoline and diesel power or alternate fuel	Reductions in HC and NO_x emissions 75% reduction with >2010 standards	LDV import certification (to PROFEPA). Expanded monitoring for HC and NO_x in major cities other than Mexico City	http://www.semarnat.gob/mx/levesynormas/Normas%20)ficilales%20Mexicana%20vigentes/NOM 042 SEMARNAT 2003 7 Sep 05.pdf
U.S. industrial sources					
Maximum Achievable Control Technology (MACT) Program	2007	Nationwide industrial sources of organic hazardous air pollutant emissions	Projected VOC reductions of 2.4 million t/year (from all sources) and NO_x reductions of 168,000 t/year (from major stationary engines) by 2007	Design for emission testing of selected sources for NO_x and speciated VOC (including relevant HAPs). Design for specialized intermittent (regularly) scheduled studies near specific sources to monitor changes expected in VOC and NO_x emissions, as well as some diesel or industrially related HAPs. Explore opportunities for local exposure-health effects studies of subpopulations near sources	http://www.epa.gov/ttn/atw/

Table 8.2 (continued)

Major initiative	Implementation period/compliance date	Affected sources	Projected emission reductions (<u>Actual reductions underlined</u>)	Monitoring implications/accountability tests	Background information (spatial domain, compliance dates)
Mexican industry					
Sulfur recovery from oil refining	Recovery >90% by Feb. 28, 2008 in Cadereyta, Cuidad Madero and Tula; Mar. 1, 2008 Salamanca; Jan. 1 2010 Minatitlan and Santa Cruz	6 PEMEX refineries listed	Sulfur recovery 90% relative to 2007 levels. Sulfur emissions from refineries installed after March 2008 will be lower than 5% of 2007 average emissions	PEMEX emission reports periodically to PROFEPA. Potential for expanded sulfur monitoring near sources for verification of sulfur emission levels	http://www.semarnat.gob/mx/leyessynormas/mor,masoficialesmexicanasvigentes/Atmosfera/NOM%20148%20SEMARNAT%202006%20CONTAMINACION%20ATMOSFERICA%20RRCUPERACION%20AZUFRE%20DE%20PROCXESOS%20DE%20REINACION%20PETROLEO.pdf

[a] Delayed pending legal challenges

tion. Programs directed at HAPs have included those related to the transportation sector and a variety of industrial and commercial sources of concern. Over the same time period, analogous programs have been put in place in Canada and, for CPs, in Mexico.

One difficulty with incorporating HAPs into existing air quality management strategies designed to address CPs is the significant overlap between HAPs and VOCs or PM. Numerous HAPs, such as toluene, benzene, methanol, and formaldehyde, are themselves grouped in the generic VOCs. Many of these are photochemically reactive and play a potentially large role in the modeled atmospheric chemistry. In addition, some HAPs, such as manganese, nickel, chromium, and cadmium, are PM components. Inconsistencies between VOCs included in HAP inventories and those included in CP inventories have a larger impact on an multipollutant framework than inconsistencies between PM and PM HAPs inventories because (1) VOC HAPs can constitute a large fraction of VOC mass relevant to CPs (mobile source VOC is approximately 25% HAPs, for example); and (2) some VOC HAPs, such as formaldehyde and acetaldehyde, play a direct role in the atmospheric chemistry. Because of inconsistencies in the emissions between the HAPs, VOCs and CP related VOCs in the emission inventories and in the speciation profiles used in modeling, different modeling results could occur when bringing HAPs into a modeling framework. The inconsistencies could be important, as in one case in which hexane emissions in the U.S. inventory were estimated as 3,600 tons, but total VOC emissions (including hexane) were estimated as only 160 tons. This illustrates one example of the ambiguities faced by air quality managers in developing multipollutant strategies.

Comparison of projected emission reductions to actual changes in emissions tends to be more straightforward for stationary sources than for mobile sources, as may be seen by inspecting the listings in Table 8.2. Pollution controls are introduced in new vehicles, which then enter the fleet at varying national and local rates depending upon the renewal rate of the light and heavy duty vehicle fleet. The fleet changes can also overlap with changes in fuel composition and with further changes in vehicle emission control technologies, making it very difficult to distinguish the effects of specific programs. Evaluating the extent to which these programs have been successful may require the types of top-down evaluations of emissions described in Chap. 8 of the EIA and in the kinds of studies such as done by Parrish et al. (2002) and NARSTO (2005).

Next we discuss two major initiatives in somewhat more detail to illustrate the current management strategies for reductions based on the existing U.S. single pollutant framework. The two initiatives are the introduction of catalytic converters in light duty motor vehicles, and the acid rain program under Title IV of the 1990 CAAA. The widespread use of catalytic converters for reduction of CO, VOC, and NO_x emissions is followed by a summary of the 1990 acid rain provisions to reduce SO_2 and NO_x emissions from coal-fired power plants, mainly east of the Mississippi River. The purpose of these discussions is to identify key points that enabled the programs to be successful initiatives as guidance for future program designs, including considerations of accountability.

8.3.1 Catalytic Converters in Motor Vehicles

The introduction of the catalytic converter for light duty motor vehicles is one of the earliest examples of a regulatory strategy designed to manage emissions of multiple pollutants. The converter's oxidation catalyst was designed to more fully oxidize unburned hydrocarbons and CO to H_2O and CO_2. The catalytic converter was later improved to reduce NO and NO_2 to N_2, in what is commonly known as the three-way catalytic converter. This is one of the earliest regulatory programs developed by EPA, and provides several examples of the issues associated with a multipollutant, accountability approach to air quality management. The state of California played a key role in pushing for development and use of catalytic converters by setting aggressive motor vehicle emission limits in the 1960s (O'Connor 2006).

The first issue was the recognition that the combustion process in motor vehicles can emit two products of incomplete combustion (CO and VOC) that can be controlled using the same basic approach—oxidation to more fully complete the combustion process. After initial mobile source emission limits were set by EPA in the early 1970s, the development of a catalyst to oxidize CO and VOCs in the exhaust stream provided an effective strategy for achieving the emission limits (Palucka 2004). However, the presence of lead (and later high sulfur content) in gasoline as an anti-knock agent resulted in poisoning of the catalyst and, if not addressed, an ineffective pollution control strategy. The second issue was the need to recognize the impacts of the complete mix of constituents in the exhaust if a successful control strategy is to be developed. In this case, the recognition of catalyst poisoning resulted as an element in EPA's first steps to remove lead from gasoline (see also Text Box 3.4), even though the intent of catalytic converters was to reduce products of incomplete combustion (CO and VOCs).

In 1972, EPA mandated that each gasoline supply station provide at least one pump for lead-free gasoline. Although there had been growing evidence of serious health impacts due to exposure to airborne lead, the lead-free pump requirement was actually set primarily to protect catalytic converters, which were introduced by automobile manufacturers to oxidize CO and VOC emissions. Even though regulations specifically designed to remove lead from gasoline for the purpose of directly reducing exposure to lead were not promulgated until 1977, the reduction of lead to enable ambient CO and HC reductions resulted in measurable reductions in total emissions and ambient lead concentrations by 1975. By 1986, EPA had lowered the allowable amount of lead in gasoline to 0.1 gm/gal from the 1.7 gm/gal allowed in 1975. One of the more innovative aspects of these reductions at the time was the use of tradable lead credits allocated to refiners based on the amount of lead removed from their products (EPA 2001). Lead was prohibited from use in gasoline in Canada in 1990 by the Gasoline Regulations, promulgated under the Canadian Environmental Protection Act (CEPA). The Regulations, which assured the use of virtually lead-free gasoline in Canada, were enacted to address health concerns associated with low-level exposure to lead (EC 1989). Mexico began requiring reduced lead gasoline in 1986 (Bravo et al. 2006), introduced unleaded gasoline in 1990 (Lovei 1997), and banned leaded gasoline in 1998.

Oxidation catalysts were required on new automobiles and light-duty trucks beginning in 1975. The three-way catalyst was required in California beginning in 1980 (O'Connor 2006), and nationally in 1981 as the industry gained manufacturing and operating experience with the oxidation catalyst and with advances in catalyst capabilities. Canada adopted catalytic converters later in the 1980s while using alkyl manganese as an interim substitute for lead. Even later, two-way catalysts were adopted in Mexico in 1991 and three-way catalysts in the 1993 model year.

The success of the three-way catalyst depended upon more than simply installing the catalyst in the exhaust stream. The system relies upon maintaining a consistent oxygen level in the exhaust, which in turn requires sensors and continuous feedback to control air and fuel flow. In this configuration, the three-way catalytic converter represents a truly multipollutant control system.[4] Because the replacement rates of the vehicle fleet are relatively slow, the technology was not in full use for nearly a decade. However, despite increases in vehicle miles traveled, CO emissions from passenger cars and light-duty trucks is estimated to have decreased from just under 134 million t/year in 1975 to approximately 99 million tons in 1990, a 26% decrease. As discussed in detail in the EIA, this reduction is generally consistent with ambient CO measurements after 1980, although discrepancies remain to be completely resolved. The same discussion noted that NO_x emissions have likely increased in the period between 1990 and 2000, but the contribution of NO_x from off-road engines is a confounding factor (NARSTO 2005). VOCs are estimated to have decreased from 13.3 million t/year in 1975 to 8.3 million t/year in 1990, a decrease of approximately 38% (EPA 2007a).

It is difficult to quantify the emission reductions due to catalytic converters alone, particularly in later years, due to the introduction of reformulated gasoline (RFG), which resulted in increased O_2 in the fuel through the use of additives such as methyl-tributyl ether (MTBE) and ethanol. EPA estimated that RFG would result in the reduction of 105,000 tons of VOCs and NO_x (see Table 8.1), and additional reductions of HAPs from vehicles (EPA 1999). A more recent study suggested that the majority of reductions in CO, VOCs, and NO_x have been the result of improved vehicle emission control systems (Bishop and Stedman 2008). The simultaneous improvement in engine technologies, introduction of RFGs in different locations and at different times, and implementation of inspection and monitoring programs confound the ability to determine the reductions associated with the different components of the mobile source emission control programs.

A third point to be emphasized in this case is that it was necessary to evaluate the process from a systems perspective to develop a successful strategy. Without considering the fuel supply system as an integral part of the broader process, the ultimate goal of reducing CO and VOC emissions could not have been successful. This program required that the sources add new control technology (the catalytic converter) and that they use a different fuel (unleaded gasoline) to allow the control technology to work as required (EPA 1999).

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[4] One limitation of the exhaust catalyst use is that it emits traces of reduced sulfur and NH_3 under some conditions, which amounts to a multipollutant disbenefit.

The final point to emphasize is that the estimates of mobile source emission changes depend on the consistency of the varying emission models used. Chapter 8 of the EIA (NARSTO 2005) discusses several examples of how past-year emission estimates changed as different emission models. In one example, the EIA noted that EPA's 2003 estimate of 1980 CO emissions from on-road vehicles was about 80 million t/year, compared to over 140 million t/year for on-road vehicles in 1980 in EPA's 2004 estimate (Parrish et al. 2002; NARSTO 2005). This "artificial" increase for 1980 was attributed by Parrish et al. to the use of a more recent version of the MOBILE emission model, MOBILE6, relative to earlier versions. Changes were also noted for NO_x and selected VOCs in other examples, and the EIA illustrated approaches using ambient measurements to evaluate the inventory data to determine whether trends in ambient concentrations could be used to inform inventory development.

The changes in model results relative to one another make it difficult to evaluate long-term trends in emissions, although emission estimates are provided for past years in EPA's Trends Reports (e.g., EPA 2003), with all years in a given Trends Report being estimated using a single version of the emission model. From the perspective of accountability, however, projected emission reductions made at the time a regulatory program is implemented and actual emissions need to be compared on a consistent basis if reliable estimates of regulatory performance is to be reported. Otherwise, current emissions and projected emission reductions are estimated using different methods and meaningful comparisons are not possible.

In summary, the introduction of catalytic converters required several key issues to be recognized and addressed: (a) the combustion process is inherently multipollutant, which allows several pollutants of concern to be reduced using a single technology (e.g., CO, VOCs, and NO_x with a three-way catalyst, or for stationary sources, PM and HAPs [using fabric filters]or SO_2 using scubbers or fuel desulfurization); (b) the potential for exhaust gas constituents that are not of immediate interest can affect the ability to control those pollutants that are targeted for reduction; (c) the entire system, from fuel to fuel combustion to exhaust gas treatment, is connected and where changes can be made most effectively to reduce ultimate emissions; and (d) development of baseline emission data to which post-program changes can be compared and to maintain comparable measurements and models so that actual emission changes can be compared on an equal basis with the projected changes (e.g., Zavala et al. 2009b). The baseline and subsequent comparable measurements can be either of ambient concentrations (as in the case of CO noted above) or of emissions (as for SO_2 as discussed below).

8.3.2 Acid Rain Provisions of the Clean Air Act Amendments of 1990

The emission reductions required by Title IV of the 1990 CAAA were aimed at SO_2 and NO_x reductions. The SO_2 emission reductions were mandated through the use of tradable allowances. Beginning in 1995, coal-fired electric utility boilers mostly in the eastern United States were required to reduce annual SO_2 emissions by 4 million tons compared to 1990 levels. From a total of 15.2 million t/year in 1990, coal-fired utility boilers reduced SO_2 emissions to 11.6 million t/year in 1995 and further to 9.7 million t/year in 2002 (EPA 2007d). Through the use of tradable allowances for SO_2, shifts to low-sulfur coal, and emission controls, the Acid Rain Program achieved greater reductions than were required at a lower cost than projected (Kerr 1998). Nevertheless, installation of flue gas desulfurization (FGD) systems remained a significant option for emission reduction. In 1990, 69.1 gigawatts (GW) of U.S. coal-fired electricity generating capacity were equipped with FGD systems. By 1995, that number had risen to 84.7 GW, and by 2002, to 98.4 GW. In 2005, over 101 GW of coal-fired generating capacity had FGD systems, out of a total of 309 GW (U.S. DOE 2007).

EPA has also estimated the NO_x provisions of CAAA Title IV to have reduced emissions by 3.3 million tons below 1990 levels. These estimates are based on continuous emission monitor (CEM) measurements, and are consistent with reductions in ambient airborne odd nitrogen concentrations and nitrogen deposition measurements (EPA 2007b). However, the environmental responses to NO_x emission reductions are not as easily attributed to the Title IV requirements for utility boilers as are similar responses for SO_2, due to the fact that NO_x emissions are associated with a wider range of sources than SO_2, including mobile sources.

The CAAA Title IV trading provisions also resulted in the installation of CEMs for SO_2 and NO_x emissions at all plants covered by the Acid Rain provisions. The installation of CEMs provided emission data that could be used to support the financial transactions of the allowance market, and also provided high-quality emission measurements. These data have proven to be well suited for comparisons over time, enabling air quality managers to clearly determine the performance of the program, and support trend comparison with ambient concentrations (see also Chap. 12).

Although on the surface the Acid Rain provisions considered SO_2 and NO_x separately, in practice plant operators recognized the need to understand the impacts that new technologies or fuels would have on both pollutants (as well as other pollutants such as PM and on plant operations). Switching to low sulfur coal for SO_2 control, for instance, can impact the performance of low NO_x burners due to increased slag buildup and changes in boiler temperatures. Similarly, application of low NO_x burners can result in higher PM emissions due to higher levels of unburned carbon (Nordin et al. 1997). In the context of the current discussion, the key lesson of the Acid Rain program is the ability to accurately determine emissions because of the use of CEMs and the quarterly reporting of emission data. This requirement provided air quality managers with accurate data relatively quickly, allowing the benefits of the program to be evaluated promptly (see also Chaps. 6 and 12).

The increased use of FGD systems is also important from the perspective of mercury control, due to the ability of oxidized mercury to be captured in the FGD systems. Although it is not possible to accurately estimate the level of mercury removal associated with the increased use of FGD systems to meet the Acid Rain provisions of the CAAA, it is likely that mercury emissions from coal-fired utility boilers have been lowered because of the greater extent of FGD use since 1990. Mercury, however, continues to be a pollutant of concern. Due to recent court decisions in the United States, which reinforce the designation of mercury as a HAP, it is likely that further reductions in mercury emissions from coal-fired power plants may require consideration of maximum available control technology (MACT). This decision could have major ramifications for stack effluent controls well beyond the use of FGD systems and particulate controls.

8.4 Looking Forward: Inventory Requirements in a Multipollutant-Accountability Context

While it is instructive to look to past experience, retrospective evaluations of emission controls are useful only to the extent that they verify at least qualitatively the expected reductions in ambient air quality, and they inform decision-makers about needs for future management direction. In the United States, for example, several major air pollution regulations have recently been promulgated for single pollutants (*Levels 1* and *2*). In particular, the diesel regulations address on-road and off-road sources, while the CAIR focused primarily on coal-fired power plants (Table 8.2). In addition, implementation of the revised 2006 $PM_{2.5}$ NAAQS was scheduled to begin in 2008 with the submittal of State Implementation Plans (SIPs) to address conditions in non-attainment areas (see also Chaps. 3 and 4). Considerable interest exists in determining the degree of progress toward achieving the environmental goals associated with each of these actions during their implementation rather than evaluating their degree of success well after the fact. A fundamental, continuing issue then is whether the tools are available to provide robust measures of interim progress for evaluating the effectiveness of the regulations, and for applying corrective measures if necessary.

Some tools provide good, but not necessarily ideal data for determining accountability. The availability of CEMs for SO_2, NO_x provide robust emission data for evaluating the progress of emission reductions expected from U.S. power plants. However, the same continuous monitoring is not yet available for power plants in Canada or Mexico, or for industrial operations in the three countries. In addition, HAPs from power plants or industrial sources are measured intermittently, or perhaps not at all, and never for long periods of time. However, recent developments in mercury emission monitoring technologies, and the associated validation methods and calibration standards for these systems, will enable high-quality data for mercury emission reductions.

For the other major source group of pollution, transportation, comparison between projections and actual CO, VOC NO_x and PM emissions is far more difficult. Both onroad and nonroad vehicle emissions are estimated with models. Available emission models, such as MOBILE6 (or MOVES, which is expected to replace it), provide the capability to estimate changes in emissions as inputs for air quality models. However, questions remain with respect to the model's ability to provide consistent comparisons between prospective and retrospective results, given fuels, vehicle maintenance practice, complex on-road conditions and fleet turnover. Such questions become of even greater concern as the spatial and temporal scales of concern become finer. Fuels have mandated properties and seasonal and geographical transitions in all three countries. Vehicle maintenance is known to vary extensively depending on vehicle age and the reliability of mechanical work. Road and traffic conditions vary locally and are known to be simulated in an unreliable way in nationally based codes. Fleet turnovers vary depending on vehicle model and year, and economic conditions, but present rotations of light duty vehicles is probably ten years or more, and heavy duty vehicles probably longer. Emission models have evolved in much the same time scale as the air quality models, so that retrospective comparisons are generally not practical. The models do not estimate the speciated emissions of VOC or PM_x, so that special estimation procedures are needed in these cases, including receptor modeling and sampling based on laboratory dynamometer testing.

Emissions during transient operations can lead to major uncertainties for both stationary and mobile source emission inventories. Plant startup, shutdown, and upsets can also result in changes to stationary source emission profiles and mass. Cold starts and acceleration of vehicles can impact both emission mass and composition. Although considerable progress has been made regarding transient emissions from mobile sources, the impacts of transient operations in an accountability framework are not fully understood.

For fugitive and area sources, evaluating even *Step 1* accountability (emission reductions) can be problematic. Inventories for these sources, such as process leaks, agricultural activities, and wildfires, are at best highly uncertain “estimates” given the often sporadic nature, both temporally and spatially, of their emissions. Although there have been improvements in estimating these emissions using remote sensing and other technologies, extrapolating the sparsely available measurement data to provincial, state, or national emission inventories relies heavily on models of both emission and activity levels based on numerous assumptions regarding frequency and magnitude of activities and relatively few measurements compared to the number of emission events.

At accountability *Steps 1* and *2*, ambient air quality monitoring networks are well established in the United States, Canada, and Mexico City (see Chap. 10 and appendices). These provide a means of verifying emission changes, either in terms of gross emissions or speciated properties. Ambient data also provide valuable data for trends, though shortcomings in the monitoring networks are well documented, as discussed by Demerjian (2000) and by McMurry et al. (2004). Remote sensing recently has been used for roadside sampling of vehicles, and highway tunnel experiments, as well as chase vehicle sampling have been applied to verify model estimates (e.g., NARSTO 2005). With the exception of the ambient monitoring, other methods have not been used for extended time periods of several years, so that their application to accountability exercises is problematic. Beyond accountability *Step 2*, obtaining multipollutant emissions data with long-term changes has not been attempted, either in systematic design or execution. Other possible opportunities for long-term evaluation could include the use of local vehicle registration data combined with knowledge by vehicle model of fuel use per mile traveled or fuel volume, or traffic volume data on selected roads. Ambiguities increase when both exhaust and evaporative emissions are estimated.

Determining the effectiveness of pollution management strategies requires evaluation of the extent to which projected emission reductions have actually been achieved after the implementation of emission control programs. Recently, attention to such retrospective comparisons has increased for major initiatives. For example, the Acid Rain program's reliance on CEMs for SO_2 and NO_x represents an ideal situation for determining the performance of an emission reduction strategy. High quality emission and operations data are collected on a consistent and continuous basis and reported quarterly, and have been used for evaluating reductions in regional ambient sulfate concentrations and sulfate deposition (Chap. 12). Both the CAIR (EPA 2005) and CAMR programs depend upon the use of CEMs to support trading of emission allowances, and the resulting data would provide an excellent basis for evaluating the programs' performance over time in relation to ambient conditions.

For many reasons, this ideal has not been replicated for most pollution reduction programs. CEMs for mobile sources, for instance, have not been practical and so other measures of program performance must be used. In the case of catalytic converters, the first measure of accountability can be the fraction of vehicles that have the technology installed. An alternative measure of accountability could be the use of massive databases from compulsory emission tests and engine certification. Data mining exercises of those data sets could provide statistically supported estimates of catalytic converter efficiency and aging (Riveros et al. 2002). A third measure would be the (repeated over many years) estimate of emissions from a designated in-use fleet of light-duty vehicles, but these estimates depend upon the emission model used to develop the estimate. Evaluation of the performance of the recent diesel engine rules is also subject to this limitation, and further highlights the need for consistent, traceable emission models that maintain a reasonable degree of consistency in inventory estimating methods over the period of years during which the rules are implemented and beyond.

Providing accountability for multipollutant air quality management at Levels *3* and *4*, where multiple pollutants need to be identified and tracked, much greater attention will need to be given to speciation of multipollutant sources. In addition, expanded CEM capability will be required for large stationary sources at a minimum and for the transportation sector. In addition, greater attention to multipollutant fugitive and areas sources will be needed, since these kinds of sources often contain a wide range of species that could be of interest as toxins, even at low mass emission levels.

8.5 Multipollutant Control Technologies at the Source Level

From a collective source perspective, addressing multiple pollutants under a single framework is much more efficient than addressing them individually. Installation of pollution controls can require substantial plant downtime and considerable modifications to plant systems. Although different pollutants often require installation and operation of different control technologies, the installation process can be greatly simplified and costs considerably reduced if the plant is designed with systems that are integrated as a coherent, total "process". Although integrated design and installation often leads to difficulties in estimating the fraction of costs associated with the control of a given pollutant, this approach provides numerous benefits in terms of system design, operation, and cost.

The design of a pollution control system for a single pollutant cannot overlook the potential for that technology to aid in the control of other pollutants. Particle control technologies can improve the capture of most metal air toxics. Many organic air toxics can be reduced or eliminated with improved combustion processes that also reduce CO and VOCs. Water soluble air toxics can also be removed by wet FGD systems, including some forms of mercury from coal-fired power plant flue gas (Srivastava et al. 2004; Walsh et al. 2006). Conventional particle control systems, such as electrostatic precipitators and fabric filters, can be adapted to apply sorbent injection methods to reduce mercury or SO_3, but they need to be designed to handle the additional particle loading, or additional capacity must be installed later to accommodate the particles injected to control other pollutants.

Failure to take a multipollutant perspective when designing pollution control systems to address single pollutants also can result in unintended adverse impacts. An example is the formation of visible acidic aerosol plumes that can result when separate control systems for NO_x and SO_2 are not designed with a clear understanding of the response of the entire flue gas system. Selective catalytic reduction systems installed to reduce NO_x emissions tend to increase the rate of oxidation of SO_2 to SO_3. The increased flue gas moisture and reduced in-stack temperature associated with subsequent wet FGD can drive that increased SO_3 to form visible sulfuric acid (H_2SO_4) aerosol in the near-stack plume. In this situation, each control system works as designed to lead to substantial reductions in NO_x and SO_2, but the combination results in elevated levels of acid aerosol formed in the effluent, which can require an additional control technology to mitigate. Evaluating the complete pollution control system requirements and consequences in an integrated manner can help to eliminate or minimize these and similar problems.

Table 8.3 illustrates some of the major air pollution control systems available for stationary sources, and some of the impacts those systems can have on other pollutants. In some cases, these technologies provide co-control of pollutants other than those they are primarily designed to control. In other cases, emissions of other pollutants can increase if system design and operation do not consider the integrated nature of the system. A few truly multipollutant control technologies have been developed. However, many of these, such as electron beam technology, have not been successfully deployed to date in widespread commercial operations.

We have limited our discussion of multipollutant issues to air emissions. However, many control technologies transfer collected pollutant products to other media. These technologies or approaches result in generation of solid residues or liquid effluents that contain the pollutants removed from gaseous exhaust streams. Fly ash, FGD residues and scrubber water, and other waste streams must be considered

Table 8.3 Major control technology types for stationary sources and their impacts on other pollutants

Technology	Principal sources	Target pollutant	Impacts on other pollutants
Flue gas desulfurization	Electric generating units	SO_2	• Reduces soluble mercury • Reduces PM (especially larger than PM_{10})
Electrostatic precipitator	Electric generating units, industrial combustion sources	PM	• Reduces particulate air toxics (primarily metals) • Can reduce mercury when unburned carbon is present • Enable sorbent-based capture of mercury and other air toxics
Fabric filter	Electric generating units, industrial combustion sources	PM	• Reduces particulate air toxics (primarily metals) • Can reduce mercury when unburned carbon is present • Enable sorbent-based capture of mercury and other air toxics
Combustion NO_x controls	Electric generating units, industrial combustion sources	NO_x	• Can increase CO • Can increase carbonaceous PM
Selective catalytic reduction	Electric generating units, industrial combustion sources	NO_x	• Can increase sulfuric acid aerosol • Can convert mercury to oxidized forms more amenable to removal by FGD
Selective non-catalytic reduction	Electric generating units, industrial combustion sources	NO_x	• Excess ammonia injection can result in increased NH_3 emissions
Combustion CO controls	Electric generating units, industrial combustion sources	CO	• Can reduce unburned carbon in PM • Can reduce air toxics caused by incomplete combustion • Can increase NO_x
Non-thermal plasma technology[a]	Electric generating units	Multipollutant	• Designed to reduce SO_2, NO_x, PM • Can increase mercury removal in some cases

[a] Largely in the development and demonstration stage. Designs are being tested by Powerspan (2008) in the United States and Natural Resources Canada (2008)

in a complete evaluation of the environmental impacts of air pollution control. The recent breach of an ash pond in Tennessee illustrates some of the potential problems that can arise from transferring air pollutants to other media (e.g., Wikipedia 2009). Another problematic example may be the use of activated carbon adsorption of mercury in flue gas. The carbon necessarily will be removed by particle collection, and will require storage of some form at the ground (Table 8.4).

Table 8.4 Technology options for multipollutant management including greenhouse gas reduction

Technology	Principal sources	Target pollutants	Limitations
Wind power	Electric power generation	All pollutants, including CO_2	Location limited; dependent on wind; destructive to avian species[b]
Solar power	Electric power generation and building heating	All pollutants including CO_2	Location limited; not continuous; requires large areas[b]
Nuclear	Electric power generation and building heating	All pollutants, including CO_2	High capital costs; major issue of solid waste management; cooling water requirements high; potential for radioactivity release
(Gas or coal) Integrated gasification-combined cycle	Electric power generation and building heating	All criteria pollutants and HAPs; efficient CO_2 removal to be demonstrated	High capital costs; high space requirements; coal as fuel questioned
Hybrid-electric vehicles, including "plug-ins"	Transportation	Reduced NO_x, VOCs, and CO; CO_2 reduced at vehicle, but offset by electricity use	Life cycle issues including disposal of batteries; Primarily for light duty vehicles and bus transportation
Electric mass transportation	Transportation	All vehicle related pollutants	Infrastructure change in cities extremely high expense; trade offs with expanded electricity production
Demand-side management[a]	All energy use, especially electricity	Reduction in all energy related pollutants	Effective on the margin of current energy use; near term potential is significant, but long term limited

[a] Conventional terminology for application of high efficiency appliances, lighting, and heating options; management of industrial, commercial and domestic energy use for minimization, especially during high demand periods

[b] There are major questions with these technologies about energy storage and efficient access to the electricity transmission and distribution system

Distinguishing between sources that are inherently multipollutant and source categories that contain a diverse range of emitters of different pollutants is important. For sources that emit multiple pollutants from a single process (such as coal or residual oil combustion), technologies designed to address emissions of one pollutant can impact, positively or negatively, emissions of other pollutants because of how the application of the technology alters the physical or chemical character of the exhaust stream. In the second instance, where multiple processes and emission source points are closely related but separate (such as in a chemical processing facility), emissions of different pollutants are less closely interdependent, and "multipollutant control" can be achieved by controlling the sources of the different pollutants on an individual basis, often without affecting the other pollutant emissions. For example, a leak detection program in a chemical plant can lead to the reduction of fugitive emissions of several different compounds from valves and pump seals. Repair of an individual leaking valve seal will reduce emissions of the particular compound that is in the line, but will not affect emissions of other compounds from other leaks in the same plant, or emissions from other sources such as boilers and heaters.

8.6 Future Challenges

8.6.1 Linking Inventories to Health and Ecosystem Effects

Ultimately, a complete accountability approach must link changes in emissions to changes in health and ecosystem effects (Steps 3 and 4 in the accountability chain) as indicated schematically in Figs. 3.1 and 3.2. In general, the species included in inventory speciation profiles and emission measurement campaigns are those of importance to emission regulations and atmospheric chemistry, or the application of receptor models. However, a complete risk- and result-based multipollutant approach to air quality management expands the range of chemical species and particle attributes of interest to include those that have been identified by the health research community to be of concern relative to public health. Nadadur et al. (2007) discussed the links between emissions and effects, in the context of the complexities of atmospheric chemistry and transport and real-world mixtures and exposures. They noted that better speciated emission profile characterization is needed to support efforts to link emissions and effects. They also concluded that more complete knowledge of temporal and spatial variations in ambient concentrations is needed, which in turn requires more detailed information on emissions (see also Chap. 5). This knowledge can be incorporated into air quality models to provide projections of gradients in ambient pollutant concentrations. Better knowledge of concentration gradients can then be used as a basis for improved comparisons in epidemiological studies where spatial and temporal variation in health response are also available.

Present knowledge of CP emissions is generally adaptable to risk assessment at *Levels 1* and *2*. However, existing inventories often fall short of providing information that is of adequate quality to support risk assessments for the pollutants identified in the 1990 CAAA, particularly for HAPs (EPA 2007c). Adding to the challenge, emerging knowledge from human health research indicates that compounds not now listed as pollutants, e.g. certain transition metals such as vanadium and iron (Costa et al. 1997; Dreher et al. 1997), reactive oxidant species in smog such as alkyl nitrates and peroxides, and PM constituents such as semiquinones (Li et al. 2002), or ultrafine particles (Oberdorster et al. 2000; Delfino et al. 2005) may play significant roles in causing adverse effects. There is currently no regulatory driver to incorporate these PM constituents or their precursors into inventories or source measurement testing, so our ability to tie emissions to specific effects is based on a limited set of results from relatively few, often well-controlled experiments, and a presumption that the constituents hypothesized to be the key causal agents are related to PM mass in a consistent manner across an entire airshed, if not across the country.

As our understanding of health effects becomes more refined, the gap between data in the inventories and the information needed to conduct effective risk assessments will expand in the absence of a concerted effort to incorporate health-specific compounds and constituents into emission inventories. This is not entirely a shortcoming of current emission inventories. In some cases, the links cannot be made because of gaps in our understanding of the human and ecosystem responses to air pollution (see also Chaps. 5 and 6). For instance, peak emissions (and subsequent peak concentrations and exposures) may be more closely related to effects than annual average emissions (and concentrations and exposures). Receptors are exposed to mixtures of CPs and HAPs from mobile source emissions, for example, but our understanding of the effects of these mixtures and how those effects change as the mixtures change is limited as noted above. At the other end of the temporal scale, cumulative deposition over longer periods may result in sensitive human populations or ecosystems exceeding a threshold for chronic or sub-chronic effects or a critical load level for ecosystems. How these factors might change as concurrent exposure to multiple pollutants is considered will depend on advances in health and ecological science.

Until the health and environmental response questions have been more thoroughly addressed, it is difficult to estimate how well multipollutant emission inventories will support studies of effects, or to what extent reductions in emissions as measured by changes cited in the inventories are related to subsequent reductions in effects.

8.6.2 Responding to Technological Changes

One potentially important challenge to implementing management options in a risk- and results-based multipollutant framework is the increasing need to address changing energy and transportation technologies as well as their selection to address long-term factors such as climate change. Three major issues are associated with energy production and use, and the climate forcing resulting from greenhouse gas or particle emissions associated with these processes, that differ substantially from previous air quality management issues (see also Chap. 11). A summary of major technological options expected to be increasingly important in the energy and transportation sectors is listed in Table 8.4. There are no surprises in this list, but it is useful to remind ourselves of their strengths and weaknesses as potential solutions to multipollutant management issues.

The first issue is the need to consider greenhouse gas emissions over a complete life cycle of a product (such as an automobile) rather than limiting concern to the point of emissions (e.g., Graedel and Allenby 1996). Because the climate forcing from greenhouse gases acts over a global scale, it is irrelevant whether long-lived greenhouse gases are emitted directly from a process or activity or are emitted in a different location. For instance, CO_2 emitted from a fossil-fueled electricity generating station that powers an electric vehicle is no different than an equivalent amount of CO_2 emitted from a fossil-fuel-powered vehicle. In addition, the total emissions that occur during the entire life cycle leading up to (and following) the activity of interest must be accounted for when evaluating alternatives. Thus, a process that emits less at the point of the emissions, but involves significant greenhouse gas emissions in the production, operation, and disposal (life cycle) of the alternative may result in a higher total greenhouse gas emission than a process that emitted higher levels of greenhouse gases at the emission point but lower levels at the intermediate processes.

The second issue concerns the change in climate itself, and how those changes may influence future air quality. As temperature, cloud cover, and precipitation change, the relationships between emission levels and ambient concentrations will also change, especially for photochemical pollutants. In addition, changes in climate will also influence actual emissions. Warmer temperatures will result in greater use of air conditioning and drier conditions may lead to increased irrigation, both of which will increase emissions from electricity generating plants or fossil-fueled pump motors (see also Chap. 11). Although it appears that the impact of changes in climate on air quality will likely be less than changes in emissions, the influence of climate change should be accounted for when evaluating the relationships between emissions and air quality.

The third issue is the increasing potential for rapid and substantial change in technologies used in major source classes such as power generation, transportation, as well as in other sectors that are currently responsible for the large majority of air pollutant emissions. Technologies for capturing CO_2 or generating electricity from renewable energy are likely to have very different emission profiles from the technologies in use today. Electric, plug-in hybrid, and biofuel vehicles are likely to become more prevalent in the coming years, resulting in changes in the amount and composition of emissions from roadways. The development and application of these new technologies represents a major change from the previous century, in which the changes in technology for electricity production and transportation were largely associated with increasing reliability and efficiency and reduction of a well-known range of pollutants.

One example of such changes in the near term is the major increase in the production and use of biofuels for transportation. The recent 2007 U.S. energy legislation called for the production and use of 36 billion gallons of renewable fuels by 2022, much of which is expected to be in the form of ethanol [Energy Independence and Security Act (2007)]. Not only will this change the emissions from individual vehicles, it will also change the total emissions of fuel feedstock production, conversion, and transportation compared to the current fuel supply system. As one example, Crutzen et al. (2007) suggested that increased use of biofuels could lead to large increases in N_2O from fertilized corn fields as more cropland was put into production to meet the demand for ethanol, thus offsetting the benefits of reduced emissions from biofuel combustion alone. A decade ago, there would be little reason to expect that changes in motor vehicle fuels would result in changes in agricultural emissions. Similarly, Jacobson (2007) recently estimated that increased use of ethanol could result in higher air pollution-related mortality, based on changes in emission profiles coupled with changes in the atmospheric chemistry due to previous pollution control programs.

The challenge for the air quality management system is to develop the tools and data sources necessary to determine how these changes in technologies are impacting air quality. As discussed above, the emission measurements and models and ambient monitoring systems must be flexible enough to account for these changes if these tools are to be capable of providing air quality managers with the information they need to respond to those changes.

8.7 NRC Air Quality Management Objectives

Lastly, a few comments are in order regarding the recommendations of the NRC (2004) report. Several recommendations in the NRC report have important implications for emission inventories: (a) expansion of national and multistate control strategies; (b) emphasis on trading strategies where possible; and (c) tracking air quality management implementation costs. The challenges to developing and maintaining emission inventories across political boundaries were addressed by NARSTO (2005). These include ensuring consistency in data collection, analysis, and reporting; coordinating reporting periods; standardization of data formats; and providing adequate resources (personnel, funding, and infrastructure) to support development of national and multistate inventories and control strategies.

The NRC's interest in emphasizing emission trading strategies raises several inventory issues in a risk- and results-based multipollutant framework. First, trading is based upon accurate measurement of emissions. It is likely that the current approach of estimating emissions from a standard annual-average emission factor and data on plant activity (e.g., fuel consumption or product output) will not provide emission data with sufficient accuracy to support trading for different individual or groups of pollutants. Increased use of CEMs would significantly increase the accuracy of emission inventories, as has been seen for SO_2 and NO_x from electricity generating units. However, whether similar monitoring can be expanded to other source types and to other pollutants remains an open question. Even if CEMs cannot be used to monitor the emissions of interest, trading needs to be based on data collected using consistent approaches and reported in consistent manners. Current inventories are often created using data from several different approaches that are not necessarily consistent with one another.

The second key question associated with emission trading approaches is how to value the effects and relative risk of exposure to different pollutants as discussed in Chap. 4. Ideally, it would be possible to place values based upon the health and ecological risks associated with each pollutant, but our current understanding of the links between emissions and health is not developed to the degree that such values can be assigned. Even as our understanding of such relationships improves, the relative values of different pollutants could easily vary with location. As an example, the relative values of NO_x and VOCs may be different in an airshed where ozone formation is NO_x-sensitive compared to one where ozone formation is VOC-constrained [see Sect. 12.2.2; and examples in Appendix A (www.narsto.org)].

The NRC's goal of tracking the costs of air quality management implementation is equally relevant in a single- or multipollutant framework, but evaluating implementation costs in a multipollutant approach raises numerous questions. The current single pollutant air quality management approach simplifies cost evaluations, but often ignores the impacts, both positive and negative, of control technologies and approaches on pollutants other than the one being evaluated. How costs are allocated to the reductions of different pollutants and, ultimately, risks has not been adequately considered. In general, the evaluation of emission control costs has been largely disconnected from the inventory process, and therefore the incorporation of costs into inventories is at a relatively primitive state of development.

8.8 Conclusions and Recommendations

The above discussion leads to several conclusions and recommendations that can guide air quality managers as they make decisions regarding sources and emission inventories in a multipollutant/accountability air quality management framework. With respect to emission inventories, these conclusions and recommendations must be considered as an addition to those given by NARSTO (2005). Of particular importance in a multipollutant/accountability context are the EIA's recommendations that inventories be comparable and timely, to ensure that data on multiple pollutants are evaluated on a consistent basis and are updated frequently enough to reflect changes in source types, emission profiles, and operating practices.

Several conclusions can be stated from the above discussions:

1. Successful air quality management programs should consider the full range of factors that influence emissions, from fuel to end-of-pipe source emission control technologies. It may be more effective to remove a given pollutant from the fuel than to remove it from the exhaust stream, for example, or the fuel may contain trace elements that prevent otherwise effective control technologies from being applied, such as in the case of lead poisoning of catalytic converters. Consideration of the entire process rather than focusing on end-of-pipe technologies can provide air quality managers with a broader, and potentially more effective, range of strategies for achieving air quality goals.
2. Adequate instrumentation, such as CEMs or appropriately designed and located ambient monitoring systems, is crucial to successfully measuring the direct impacts of emission reduction programs. The data from CEMs has made fast and accurate evaluation of SO_2 and NO_x emission reductions from coal-fired power plants a major component of the Acid Rain and the proposed CAIR pro-

gram. Ideally, such instrumentation would allow replacement of periodic testing (which collects data for only a small fraction of a source's operations) with continuous or semi-continuous measurements.

3. Efforts to develop complete accountability of emission reduction programs must recognize the shortage of significant interactions and understanding between the health/ecosystems effects communities and the inventory/emission characterization communities, as well as the considerable differences in motivation between these two groups. Because the inventory community may be focused on providing information specified by regulation, emission data on specific trace compounds of greatest interest to the health/ecosystem communities can be ignored due to resource limits or a lack of recognition of the potential importance of those compounds. Increasing the emphasis on accountability would narrow the gap between information collected for scientific evaluations and that collected to meet regulatory requirements.
4. Substantial and projected technological changes such as response to climate change and CO_2 mitigation will put additional stress on inventories and air quality management decisions. As new energy sources, end use technologies, and practices are developed and deployed, the variety of emitting sources will increase and the emissions from those sources are likely to be considerably different from the current mix of sources and pollutants. These changes will likely occur quickly and on a much larger scale relative to past technology changes as state and federal governments and industries respond to climate change. These changes will require air quality management strategies to be designed to allow periodic evaluation of assumptions and measurement of progress.

From the conclusions and discussions above, there are a series of recommendations that will guide decision-makers toward improving the ability of air quality management programs to demonstrate accountability in a multipollutant management framework. These recommendations are:

1. Address the EIA (NARSTO 2005) recommendations, particularly those related to reducing uncertainties, data compatibility, and development of new and improved tools. Improving inventories in general will contribute substantially to providing the data needed to demonstrate the accountability of regulatory programs as well as to develop multipollutant air quality management control strategies.
2. Maintain and improve current emission source profiles to reflect as accurately as possible current mixes of source types, technologies, and operations. Emissions source profiles are crucial to accurate source apportionment, which is a key tool for linking ambient concentrations to source emissions. Emissions source profiles need to be up-to-date and based upon a representative sample of sources within each category to reflect a range of emission compositions. Effective accountability requires that the source-to-ambient link be evaluated accurately, and outdated or incomplete source profiles make such evaluations more difficult and less informative.
3. Maintain data comparability over time. Developers of updated or new measurement methods, inventories, or databases need to ensure that the integrity of the

data sets is maintained as new updates are developed and implemented. As methods and models change, it is important to retain the capability to compare original projections with current emissions to determine the extent to which emission reduction programs are making progress toward the programs' goals. This may be accomplished by using overlapping calculations for some years with both older and newer methods to retain the capability to evaluate trends in emissions.

4. Incorporate a systems approach to the development of air quality management strategies. The interdependence of fuels and control technologies, linkages between different source types, and cross-media impacts require that air quality managers have a good understanding of the entire system that impacts and is impacted by control strategies. Effective control strategies may require the reduction of other pollutants first, or may imply the need to avoid an approach because of its multimedia impacts. To the extent possible, these interactions need to be incorporated into strategies that are otherwise focused on emissions from specific source types.
5. Recognize and improve knowledge on the relationships between inventories and health studies. Although epidemiological studies typically compare health measurements to ambient concentrations, the goal of many health studies is to link effects with specific source types. Developers of inventories and source profiles need to remain aware of the compounds that are being considered as important to health effects when evaluating the scope of emission sampling and analysis programs. Compounds that may not be listed as pollutants from a regulatory perspective may be of greater importance from a health effects perspective, and more complete information on the sources and amounts of emissions of these compounds can help to determine the degree to which specific hypotheses are possible.
6. Obtain additional information on control technology cost and performance. Effective management of air quality will include an understanding of the costs and benefits of the management strategies. While evaluations of the benefits are typically based on health and ecosystem impacts, the costs of implementation are almost entirely related to the sources. Inventories and other source-related data that incorporate current and thorough control technology cost evaluations can provide crucial information to the air quality management decision making process.

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Chapter 9
Atmospheric Modeling

Christian Seigneur and Robin Dennis

Air quality models (also referred to as atmospheric chemical transport models and, in the case of ozone and PM, photochemical models) simulate the atmospheric concentrations and deposition fluxes to the Earth's surface of air pollutants by solving the mass conservation equations that represent the emissions, transport, dispersion, transformations and removal of those air pollutants and associated chemical species. Figure 9.1 presents a schematic overview of the major components of a multipollutant air quality model. Contemporary air quality models can be grouped into two major categories: (1) models that calculate the concentrations of air pollutants near a source (source-specific models) and (2) models that calculate concentrations of air pollutants over large areas ranging from an urban area, to a region, a continent and the globe (grid-based models).[1] A few models combine both modeling approaches in a hybrid formulation suitable for *Level 1* and *2* applications, and perhaps to *Level 3* as described in Chap. 3.

Air quality models can be applied to a variety of spatial and temporal scales. Source-specific models such as plume and puff models are typically applied up to 50–150 km from the source,[2] whereas grid-based air quality models range from the urban scale (>4 km) to regional, continental, hemispheric, and global scales (see Chap. 11 for a discussion of hemispheric and global scale modeling). Inputs to air

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[1] Source-specific models are Lagrangian models, which treat atmospheric dispersion as a source-specific process (i.e., the dispersion coefficients are a function of distance from the sources) whereas grid-based models are Eulerian models, which treat atmospheric dispersion as a characteristic of the ambient environment (i.e., dispersion coefficients are not related to any source characteristics). Source-specific Lagrangian models include steady-state Gaussian plume models such as AERMOD and non-steady-state puff dispersion models such as CALPUFF and SCICHEM.

[2] Neighborhood scale calculations <1 km^2 are much smaller than the resolution of grid-based models. Estimation of concentrations in this range require merging of plume models with the larger scale calculations.

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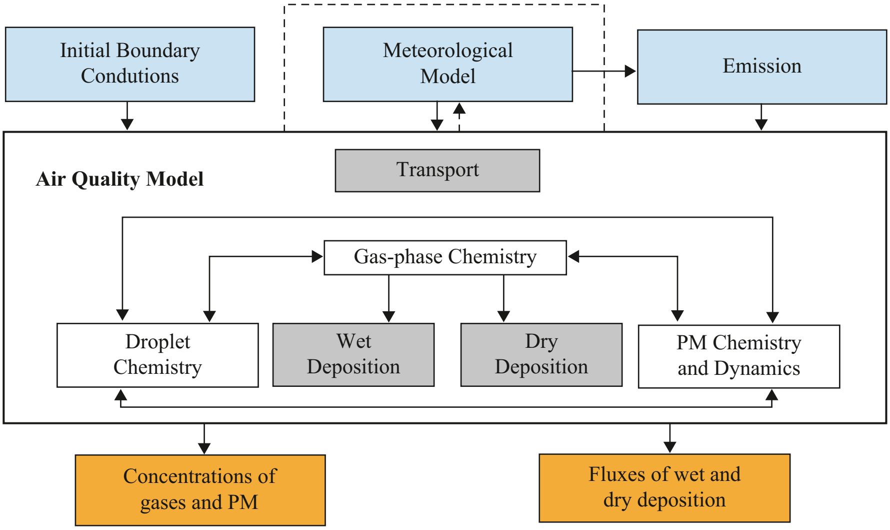

Fig. 9.1 Schematic description of an air quality model; the *dotted line* and *arrow* correspond to the case where both meteorology and air quality are simulated jointly

quality models include the emission rates of primary air pollutants and precursors of secondary air pollutants, meteorology (three-dimensional fields of winds, turbulence, temperature, pressure, boundary layer height, relative humidity, clouds and solar radiation), and boundary conditions (baseline or background conditions in the case of source-specific models; see Fig. 9.1). For grid-based models, an emission model is used to translate an emission inventory into a spatially distributed and temporally resolved grid structure. Inventories identify point sources and area sources within grid-geographic locations. For example, on-road mobile source emissions must account for vehicle fleet composition, vehicle speed, and ambient temperature as a function of time and road type. Biogenic emissions are a function of land use, season, ambient temperature and solar radiation. Emission inventories and models are discussed in Chap. 8. Meteorological conditions are obtained from observational data or from the output of a model (or a combination of both). In advanced research-grade models, both meteorology and air quality are simulated jointly so that the chemical composition of the atmosphere can influence the meteorology (e.g., the effect of particulate matter on atmospheric radiation); examples include the Multiscale Climate and Chemistry Model (MCCM; Grell et al. 2000) and the Weather Research and Forecast model with chemistry (WRF-Chem; Grell et al. 2005). When models are simulating a combination of several spatial scales, the calculations need to downscale meteorology from global to synoptic scale or to regional/urban-neighborhood scale. Such downscaling can be challenging when forecasting future climatology, which is needed to address the effect of climate change on future air quality and atmospheric deposition due to changes in air concentrations, precipitation and possibly also land use (see Chap. 11). The effect of future climate change also will need to be reflected in the emissions (see Chap. 8). Boundary conditions for downscaling to regional-scale models (~10–40 km resolution) are now typically generated from larger-scale models. Such approaches, although ultimately dependent on the quality of the global emission inventory, reduce the uncertainty in the estimation of boundary conditions for finer scale resolution, particularly those above the planetary boundary layer (e.g., Appel et al. 2007).

Although air quality models have been applied historically to address issues specific to ambient air quality standards (i.e., one criteria pollutant at a time) or welfare (e.g., acid deposition or visibility impairment), they are inherently multipollutant based. Therefore, in principle air quality models can be applied in the context of integrated emissions control programs that are designed to optimally address all of the above air quality issues simultaneously. Limitations arise, however, as additional chemical species of concern are identified that are not currently treated in air quality models. Such cases require the compilation of emission inventories and boundary conditions for these new chemical species and the addition of chemical and physical mechanisms in the model to treat their transformation and deposition.

9.1 Atmospheric Modeling for Exposure Assessment

9.1.1 Needs for Exposure Modeling and Health Effects

The estimation of the health effects of air pollution requires knowledge of the concentrations of air pollutants to which an individual or a population cohort is exposed (see Chap. 5). These concentrations can be measured or calculated with an atmospheric model. Because individuals are exposed to different air pollutant levels as they move through different environments during their daily activities (e.g., home, vehicle, office, school, outdoor), one would ideally want to have high spatial and temporal resolutions of the air pollutant concentrations. The needs for exposure characterization and health effects estimation may be categorized as follows.

Spatial Resolution Some health effects studies, such as time-series mortality studies, do not necessarily require fine spatial information on air pollutant concentrations because they deal with information at the urban area or sub-urban/neighborhood level. However, a statistically based estimate of individual-level health effects requires fine spatial information on the air pollutant concentrations. The spatial resolution provided by an air quality model then needs to be sufficient to resolve the spatial variability of outdoor air pollutant concentrations so that (1) outdoor exposure of individuals and population cohorts can be assessed with sufficient spatial resolution and (2) micro-environmental models for indoor exposure have the needed outdoor concentration inputs (Isakov and Ozkaynak 2007).[3] The require-

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[3] The spatial resolution of the model output is typically coarser than the grid spacing because a grid model resolves horizontal features only at about four times the grid spacing.

ment for fine spatial resolution is greatest near sources of pollutants because the concentration gradients are strongest near those sources (e.g., near an industrial site, near a roadway). The entrainment of fresh emissions into the ambient air affects the emitted as well as the ambient pollutants through chemical reactions. For example, ozone concentrations are depleted near power plants and roadways because of the rapid reaction of the emitted NO with ambient ozone.

Temporal Resolution The requirement for temporal resolution for exposure calculations may be very fine (e.g., minutes to an hour for acute exposures), but such resolution is typically provided by micro-environmental models. The temporal resolution needed from the air quality model therefore must be sufficient to provide the needed inputs to the micro-environmental calculations. Such temporal resolution must be able to capture the temporal variability of the air pollutant concentrations. Continuous measurements of gaseous and particulate chemical species provide indications of the temporal evolution of the concentrations of primary and secondary air pollutants. For example, fluctuations in the wind (i.e., turbulence) and in the source activity (e.g., vehicular traffic) near a source lead to strong temporal variability in chemical species concentrations at a given location (Thoma et al. 2008; Baldauf et al. 2008). It is generally considered that hourly concentrations provide the desired temporal resolution for air pollutant concentrations in the ambient atmosphere. However, in some instances temporal resolution of 1, 5, 10 or 15 min may be desirable for special studies of acute exposure. In those cases, the temporal resolution of the emissions and local meteorology needs to be compatible with the selected temporal resolution of the air quality and exposure models. Alternatively, the sub-hourly variability in air pollutant concentrations due to meteorological and source variability can be treated in a statistically based uncertainty analysis (see below) rather than in deterministic calculations. Some exposure models require probability distributions of the exposure concentrations; there is then a requirement to translate deterministic output, even on fine scales, to probabilities. The development of probabilistic air quality model outputs is discussed in Sect. 9.4.

Temporal Duration Longitudinal epidemiological studies require exposure information on the relevant air pollutant concentrations over long time periods (multi-years). Time-series epidemiological studies address acute effects and may also require information on air pollutant concentrations over multi-year periods to have sufficient statistical power.

Chemical Species and Particle Size Chemical species of interest to the exposure and health effects community include the regulated species (i.e., criteria pollutants and hazardous air pollutants) as well as other chemical species considered as potentially harmful to human health. Consequently, they are investigated in terms of exposure, epidemiological and toxicological studies. Ultrafine particles (i.e., those particles less than 0.1 μm in aerodynamic diameter) are one example of a non-regulated fraction of PM that is being investigated as a potential cause of adverse health effects. Exposure to particles depends on size and chemical composition as a function of size; therefore, quantitative information from an air quality model incorporating these PM properties will lead to more complete exposure estimation. Since the indoor component of PM exposure depends on size-dependent infiltration into buildings, the outdoor estimates can be used as a component of micro-environmental models as well.

9.1.2 Current Status of Atmospheric Models

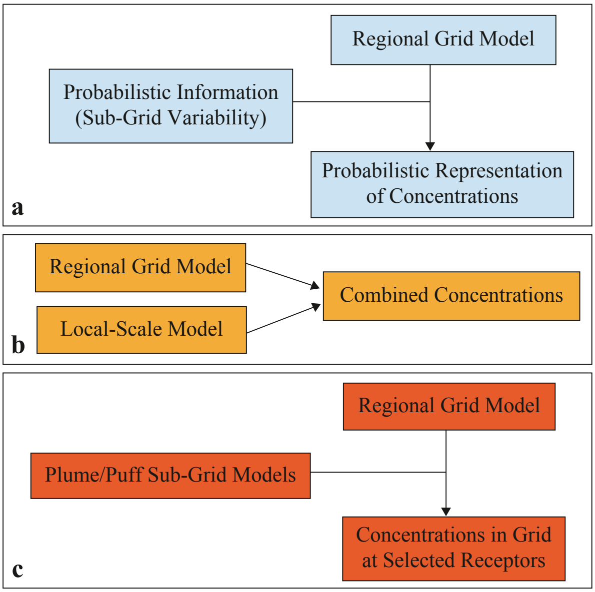
Current atmospheric models calculate the outdoor concentrations of air pollutants as a surrogate for exposure. Human exposure is known to depend not only on outdoor conditions but also indoor conditions as well, including residents, office and commercial buildings and transportation elements. If indoor sources of pollutants are known or negligible, concentrations of air pollutants in indoor environments can be calculated from outdoor concentrations using micro-environmental models. We discuss below whether current atmospheric models are suitable to address the needs of the exposure and health sciences communities.

Spatial Resolution Regional models can cover large areas but their grid spacing is constrained to 1 km or more and, therefore, they provide spatially averaged concentrations that may not be representative of the actual concentrations that may occur, for example, in the vicinity of emission sources (the formulation of some parameterizations must be modified as the spatial resolution of the model increases, e.g., convection, turbulent diffusion). Source-specific models offer a spatial resolution of a few meters if needed but they are typically limited to about 50 km from point sources and a few hundred meters from line sources. However, a few source-specific models can provide very fine spatial resolution near the source and also apply to long distances. Nevertheless, it is not practical to use source-specific models for an area with a large number of emission sources as the treatment of many sources with such models become computationally prohibitive. Therefore, a combination of a grid-based model that provides air pollutant concentrations over a large domain with a relatively coarse grid spacing (1 km or more) and source-specific models that provide information on the spatial gradients in the vicinity of major emission sources is needed to address the needs articulated above.

Touma et al. (2006) addressed the issue of representing air pollutant concentrations with fine spatial resolution over large areas. They identified three major approaches for estimating air pollutant concentrations at the sub-grid scale level within a grid-based air quality model. Figure 9.2 depicts the general features of those approaches.

The first approach (Ching et al. 2006) is solely based on a grid model but it uses finer grid resolution than generally used (e.g., down to 1 km whereas minimum grid size in urban areas is typically 4–5 km). Then, the concentrations calculated by the

Fig. 9.2 Schematic representation of three major approaches to modeling air pollutant concentrations at the sub-grid scale within a grid-based air quality model. (Source: Touma et al. 2006)



fine grid model are used to construct a distribution of concentrations over a larger grid cell (e.g., a set of 16 concentrations for a 4 km×4 km grid cell). This concentration distribution represents the variability of the chemical species concentrations within that grid cell (actually, it may still under-represent the full variability because concentrations may not be homogeneous at scales below 1 km). Such concentration distributions can be used to construct generic concentration distributions that would be a function of the chemical species, the land use category (e.g., urban, suburban, non-urban) and time (e.g., season, day of the week, hour of the day). Those generic distributions are then available to complement the results of a grid-based simulation of chemical concentrations by providing for each grid cell a probability distribution function that characterizes the variability of the modeled concentration.

The second approach uses a grid-based model and a source-specific model separately for the simulations of different sources and combines the results of the two models to construct chemical concentration fields due to all sources (e.g., Isakov and Venkatram 2006). This approach is theoretically correct for chemical species that are chemically inert or undergo first-order chemical reactions (i.e., linear chemistry). However, it is not strictly correct for chemical species that undergo non-linear chemistry and the uncertainty associated with this approach cannot be estimated a priori.

The third approach combines a grid-based model and a source-specific model into a single hybrid model (Karamchandani et al. 2007). The hybrid model is formulated so that interactions of emitted species treated by the grid-based model and those treated by the source-specific model are treated explicitly to take into account the non-linear chemical reactions. Thus, the modeled concentrations are theoretically correct for chemically inert species as well as for chemically reactive species with linear or non-linear chemistry. This approach is currently operational for point sources (e.g., stacks) and undergoing preliminary applications for line sources (e.g., roadways).

Applications of these different modeling approaches have been limited to date and there is a need to evaluate each approach against measurements as well as to compare those different approaches to assess their relative strengths and weaknesses.

Temporal Resolution The temporal resolution provided by air quality models (both grid-based and source-specific) is one hour because meteorological and emission inputs are typically available on an hourly basis. This resolution has typically been considered appropriate for the simulation of outdoor concentrations, which are used either as input to outdoor calculation exposure or to micro-environmental models. Finer temporal resolution is currently limited by the availability of sub-hourly emission and meteorological inputs.

Temporal Duration As discussed in Sect. 9.2.1, air quality model simulations are now routinely conducted for one-year periods, but not for multi-year periods. Multi-year emission inventories are currently under development at EPA; once these inventories become available, multi-year air quality simulations will be feasible.

Chemical Species and Particle Size Air quality models currently treat all major criteria pollutants (ozone, NO_x, SO_2, CO and PM), except lead, and some air toxics (VOCs, and trace metals). Air quality models typically treat VOCs via carbon-bond representations (e.g., CB IV and CB05 mechanisms) or representative molecules that correspond to a large group of molecules (e.g., SAPRC99 and RACM mechanisms). Only a few air toxic organic molecules (e.g., formaldehyde) are treated explicitly in the chemical mechanisms. To address air toxics VOC, some air quality models have been modified to include explicit treatments of VOC air toxics of interest such as aldehydes (formaldehyde, acetaldehyde), benzene and butadiene (Seigneur et al. 2003; Luecken et al. 2006). Table 9.1 presents the list of the air toxics treated by the EPA Community Multiscale Air Quality (CMAQ) model (Byun and Schere 2006).

Mercury is an air toxic of current interest that is currently treated in air quality models; it is of concern for atmospheric deposition and subsequent bioaccumulation (see Chap. 6; see also Sect. 9.3) rather than for population exposure via inhalation. Other trace metals treated in air quality models are assumed to be chemically inert. This assumption is appropriate for trace metals that have potential adverse health effects that do not depend on their chemical state. It is not appropriate for chromium (Cr) because chromium has health effects that depend on the oxidation state (Cr[VI)] is considered carcinogenic whereas Cr[III] is not) and it undergoes reduction–oxidation transformations in the atmosphere (Seigneur and Constantinou 1995; Lin 2004). One major limitation for the treatment of trace metals other than mercury and lead is the paucity of trace metal emission inventories that have received the scrutiny needed to ensure that they are reliable and accurate.

Table 9.1 Air toxics (HAPs) treated explicitly in CMAQ. (See the List of Terms for a complete list of HAPs)

Volatile organic compounds

Acetaldehyde[a, b]
Acrolein[a, b]
Acrylonitrile[a, b]
Benzene[a, b]
1, 3-Butadiene[a, b]
Carbon tetrachloride[a, b]
Chloroform[a, b]
p-Dichlorobenzene[a]
1,3-Dichloropropene[a, b]
Ethylene dibromide (1,2-dibromoethane)[a, b]
Ethylene dichloride (1,2-dichloroethane)[a, b]
Ethylene oxide[a, b]
Formaldehyde[a, b]
Hexamethylene 1,6-diisocyanate[a]
Hydrazine[a, b]
Maleic anhydride[a]
Methanol[a]
Methylene chloride (dichloromethane)[a, b]
Naphthalene[a]
Propylene dichloride (1,2-dichloropropane)[a, b]
Quinoline[a, b]
1,1,2,2-Tetrachloroethane[a, b]
Tetrachloroethylene (perchloroethylene)[a, b]
Toluene[a]
2,4-Toluene diisocyanate[a]
Trichloroethylene[a, b]
Triethylamine[a]
Vinyl chloride[a, b]
Xylene[a]

Metals

Beryllium compounds[a, b]
Cadmium compounds[a, b]
Chromium (hexavalent and trivalent)[a, b]
Lead[a, b]
Manganese[a, b]
Mercury (elemental, gaseous divalent and particulate divalent)[a, b]
Nickel compounds[a, b]

Volatile inorganic compounds

Chlorine[a]
Hydrochloric acid[a]

Other compounds

Diesel particles[b]

[a] One of the 187 hazardous air pollutants (http://www.epa.gov/ttn/atw/188polls.html)

[b] One of the 33 urban pollutants listed as air toxins by EPA (http://www.epa.gov/ttn/atw/nata/34poll.html)

Persistent organic pollutants (POPs) are currently not treated by air quality models. POPs are of interest mostly for atmospheric deposition (see Sect. 6.1.6) rather than for population exposure via inhalation.

Air quality models currently calculate PM mass concentrations in two main size fractions: fine PM ($PM_{2.5}$) and coarse PM ($PM_{10-2.5}$), using either modal or sectional representations of the size distributions (finer size resolution is actually provided by the modal representation and by sectional representations that use more than two size sections). PM chemical speciation includes sulfate, nitrate, ammonium, black carbon, organic compounds and “other” primary species (those “other” species include, for example, fly ash and other PM emissions from anthropogenic sources, crustal species such as soil dusts, and sea salt). In some areas (e.g., Mexico City), soil erosion leads to a significant fraction of PM_{10} concentrations and algorithms have been developed to quantify such crustal PM emissions as a function of wind velocity, surface roughness, soil characteristics and soil moisture. This representation of PM in two speciated size ranges ($PM_{2.5}$ and $PM_{10\text{-}2.5}$) is consistent with the current U.S. or Canadian air quality standards for PM. Other characteristics of PM are of potential interest for adverse health effects; for example, the number concentration of ultrafine particles, the particle surface area, the acidity of particles, the concentrations of individual elements (e.g., metals), and gaseous co-pollutant interactions. PM air quality models currently are not suited to address these characteristics (McMurry et al. 2004).

9.1.3 Evaluation of Air Quality Models

Air quality models are generally evaluated with ambient measurements of concentrations of gaseous and particulate chemical species and PM mass concentrations. This type of performance evaluation, generally referred to as operational performance evaluation, does not necessarily provide information on the ability of a model to simulate the relative contributions of various source categories or source areas (i.e., source apportionment) or to simulate the response of ambient concentrations to changes in emissions (generally referred to as dynamic evaluation). To that end, other modes of evaluation are conducted. First, we summarize the current status of air quality model operational performance for various chemical species, spatial scales and temporal scales. Then, we discuss some examples of source apportionment and dynamic evaluations.

Ozone Grid-based air quality models have been applied to simulate ozone concentrations for over three decades and there is considerable experience available for this chemical species. An assessment of our ability to address ozone air pollution was conducted by NARSTO (2000). Russell and Dennis (2000) reported a summary of model performance for ozone in the United States. The Canadian air quality models have recently been evaluated for eastern North America (Tarasick et al. 2007). McKeen et al. (2005) have described some recent ozone forecast evaluations for U.S. and Canadian models. Performance of air quality models for ozone has also been evaluated for the Mexico City area (e.g., Jazcilevich et al. 2003, 2005; Lei et al. 2007; Tie et al. 2007; see for example Fig. 9.3). Although there are still some uncertainties in our knowledge of the atmospheric chemistry leading to ozone formation (e.g., oxidation of aromatics, free radical chemistry, and odd nitrogen budget), ozone modeling is a mature field, which is unlikely to evolve significantly

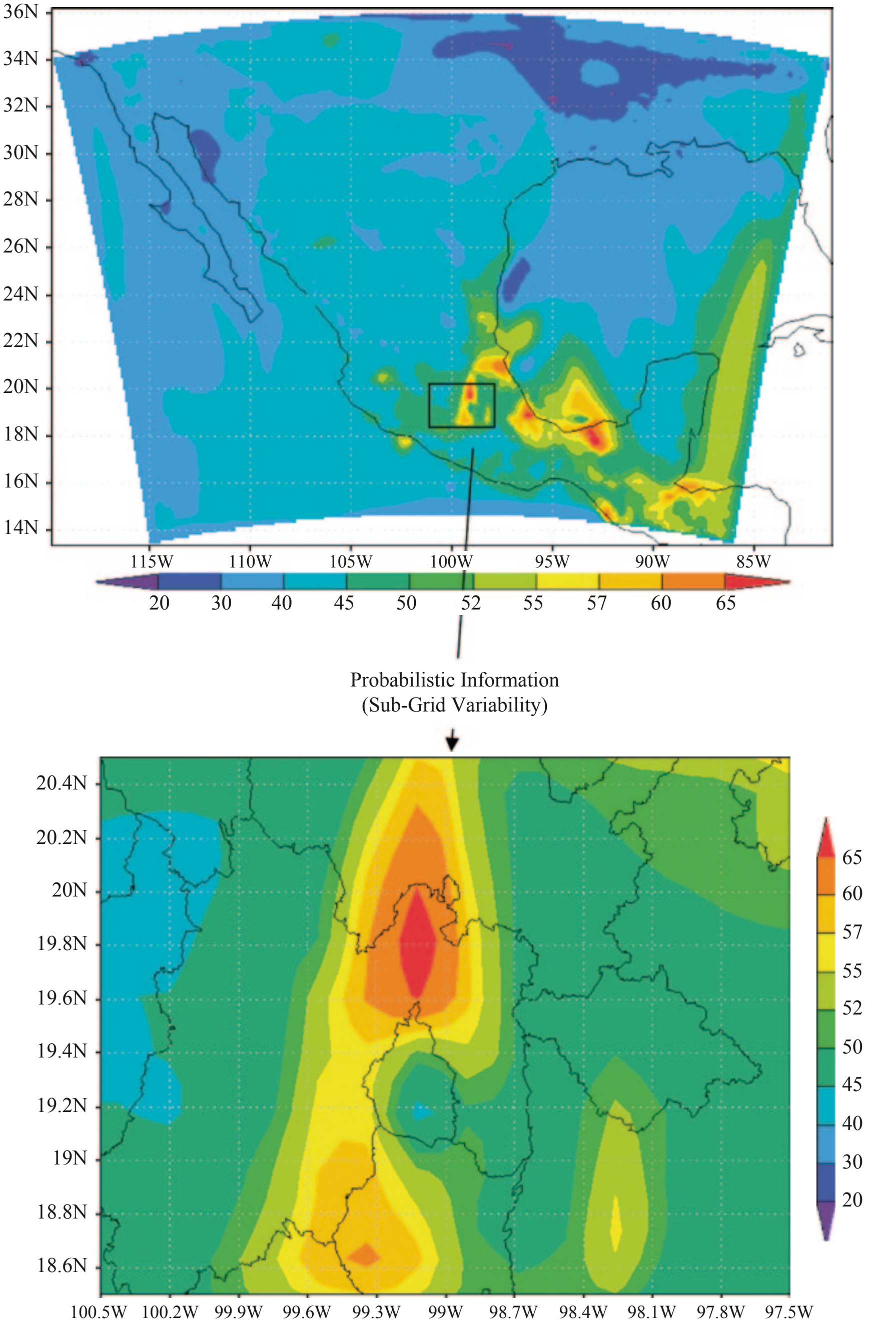


Fig. 9.3 Surface ozone concentrations simulated with MCCM for 20 March 2006 at noon over Mexico (*top*) and over Mexico city (*bottom*)

from its current status over the next few years, given a focus on a range of multiple pollutants. Overall, we can consider the ability of models to simulate ozone concentrations to be adequate for most regulatory applications. The error and bias of air quality models for 1-h average ozone concentrations are typically within 35 and 15%, respectively. However, some caution is advised when applying ozone models to predict the effect of precursor emission reductions (see also the discussion of dynamic model evaluations below).

Other Gaseous Criteria Pollutants (NO_2, CO and SO_2) Air quality models simulate NO, NO_2, CO and SO_2 as part of the atmospheric chemistry of ozone and PM formation. These chemical species are primary species (i.e., directly emitted into the atmosphere) with the exception of NO_2, which is both emitted into the atmosphere and formed in the atmosphere by the oxidation of NO (CO is also formed in the atmosphere via VOC photo-oxidation; however, the primary form dominates in urban areas where concentrations are highest). Air quality models generally perform more poorly for these primary species than for secondary species such as ozone because primary species exhibit strong concentration gradients, which are not captured by grid-based air quality models. Nevertheless, Lei et al. (2007) obtained satisfactory model performance for CO in Mexico City. Concentrations of SO_2 near point sources are typically simulated using source-specific models (point source models); thus, the spatial concentration gradients can be captured by using a fine array of receptor points where the SO_2 concentrations are calculated.

The performance of point source models has been evaluated with a variety of field data where gaseous tracers were released from a point source and measured downwind at a large number of receptor sites. The error metric used was the robust highest concentration (RHC) statistic, where the RHC represents a smoothed estimate of the highest concentrations based on an exponential fit to the upper end of the concentration distribution. For the AERMOD model (i.e., the model currently recommended by EPA for local impacts of point sources) applied to point sources with no significant downwash, the ratio of modeled to observed RHC ranged from 0.77 to 1.18 for 1-h average concentrations (four studies), from 1.00 to 1.35 for 3-h average concentrations (six studies), from 0.73 to 1.65 for 24-h average concentrations (six studies), from 0.31 to 1.65 for annual concentrations (six studies); a ratio of 1 would mean perfect agreement (Perry et al. 2005). Similarly, NO, NO_2 and CO concentrations near roadways typically are simulated with source-specific models (line source models), which can reproduce the sharp concentration gradients away from the roadway. The performance of line source models has been evaluated in several studies by comparison with measurements from five different field studies at a number of receptor sites in the vicinity of roadways. The correlation coefficients (r) ranged from 0.51 to 0.87 with 85% of the model results overall being within a factor of two of the measured concentrations (Benson 1992).

The photochemically-based models also can estimate concentration fields for VOC, including some speciation, as well as other oxidant species, including nitric acid, organo-nitrates, hydrogen peroxides and organic peroxides. The fidelity of these estimates is largely unknown, because of the rarity of ambient measurements for testing.

Particulate Matter Applications of grid-based air quality models to PM have taken place over the past two decades but most of the major model development and evaluation efforts have occurred over the past decade. An assessment of the ability of air quality models to simulate PM air pollution levels was conducted by NARSTO (McMurry et al. 2004). Seigneur (2001) has summarized early model performance evaluations for PM. More recent performance evaluation results for annual $PM_{2.5}$ are reported by Eder and Yu (2006) and Appel et al. (2008) for the CMAQ model over the contiguous United States; by Tesche et al. (2006) for CMAQ and the Comprehensive Air Quality Model with extensions (CAMx) over the southeastern United States; and by Gong et al. (2006) and Park et al. (2007) for A Unified Regional Air Quality Modeling System (AURAMS) of the Meteorological Service of Canada. McKeen et al. (2007) has reported performance characteristics for several U.S. and Canadian models applied in forecasting mode. Russell (2008) has reported results for CMAQ and CAMx evaluations compared with data from the EPA Supersites Program.

Particulate matter consists of several chemical species and model performance is typically conducted for $PM_{2.5}$ mass and the major $PM_{2.5}$ chemical components: sulfate, nitrate, ammonium, black carbon and organic compounds. Figure 9.4 illustrates results for annual average concentrations of $PM_{2.5}$ and its major components simulated with AURAMS over Canada and the contiguous United States. Model performance was evaluated against measurements available from the National Air Pollution Surveillance (NAPS) network of Environment Canada, the Speciated Trends Network (STN), and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. For this specific AURAMS 2002 annual simulation, the normalized mean errors were 37% for $PM_{2.5}$, 27% for sulfate, 44% for nitrate, 27% for ammonium, 66% for black carbon, and 85% for organics; the carbonaceous species were under-predicted compared with the measurements. The performance of CMAQ was recently evaluated against measurements available from STN (mostly urban and suburban sites) and IMPROVE (mostly remote sites) for a 2001 simulation of the eastern United States using a 12 km horizontal grid (Appel et al. 2008). For this specific CMAQ 2001 annual simulation, the normalized mean errors were 44% (STN) and 39% (IMPROVE) for $PM_{2.5}$, 40% (STN) and 34% (IMPROVE) for sulfate, 72% (STN) and 95% (IMPROVE) for nitrate, 59% (STN) for ammonium, 46% (IMPROVE) for black carbon and 49% for organics (IMPROVE). Major differences between the AURAMS and CMAQ performance results occur for nitrate (AURAMS shows better performance) and organics (CMAQ shows better performance).

In general, modeling errors for $PM_{2.5}$ mass and sulfate are typically on the order of 50% or less. SO_2 emissions are fairly well characterized, the chemistry of SO_2 oxidation to sulfate is well known and sulfate is non-volatile. Thus, sulfate PM formation is well simulated by air quality models relative to the other PM components (uncertainties in cloud and precipitation fields are the largest source of uncertainty

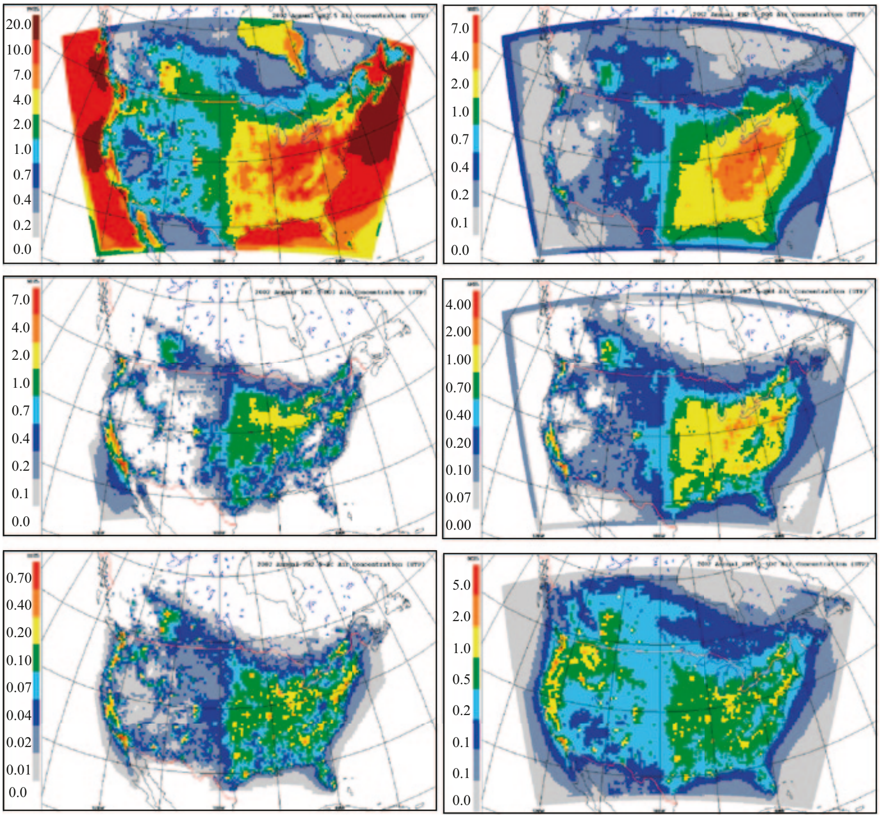


Fig. 9.4 Annual surface concentrations (μg/m^3 at STP, 0°C) of $PM_{2.5}$ and major components over Canada and the United States simulated for 2002 with AURAMS: $PM_{2.5}$ (*top left*), sulfate (*top right*), nitrate (*middle left*), ammonium (*middle right*), black carbon (*bottom left*), and organics (*bottom right*). $PM_{2.5}$ concentrations over the ocean are affected by sea salt (which is not shown as a separate component in the figure). (Moran et al. 2008)

for sulfate, as discussed further in Sect. 9.2). Performance is worse typically for nitrate and organic compounds. Although NO_x emission inventories are not as well characterized as those of SO_2, they are reasonably accurate; however, the oxidation of NO_2 to nitric acid (HNO_3) includes some heterogeneous pathways that are still highly uncertain (NO_3 and N_2O_5 reactions on particles and droplets; Davis et al. 2007) and the partitioning of HNO_3 between the gas phase and the condensed phase involves temperature and humidity, as well as the reaction with NH_3, which in turn involves uncertainties in the NH_3 emission inventories (Yu et al. 2005).

Particulate organic compounds result from primary emissions of VOCs and SVOCs and the formation of secondary organic aerosols (SOA) via VOC and SVOC oxidation. The organic compounds can be of either anthropogenic or biogenic origin. Uncertainties in the emissions of primary organic PM and SOA precursors, the chemistry of SOA formation, and the partitioning of organic compounds between the gas and the condensed phase lead to large uncertainties in organic PM concentrations. Performance for ammonium (which is associated with sulfate and nitrate) and black carbon (which is a primary PM species) tend to lie between those of sulfate and those of nitrate and organic PM.

Air Toxics Air toxics (HAPs) include a large variety of chemical compounds including principally VOC, metals, POPs and diesel particles. POPs and some metals (e.g., mercury) are mostly of concern for atmospheric deposition rather than for health effects via inhalation (see Chap. 6 and Sect. 9.2). Some model performance evaluations have been conducted for VOC simulated with grid-based models (Seigneur et al. 2003; Luecken et al. 2006; MATES-II 2000), as well as with source-specific models (Pratt et al. 2004; MATES-II 2000). Using a 4-km grid resolution, a grid-based model showed an error of 64% and a coefficient of determination of 0.25 for benzene concentrations in New York (Seigneur et al. 2003). Using a 36-km resolution over the continental United States, a grid-based model reproduced episodic and seasonal behavior of the pollutant concentrations at many measurement sites satisfactorily but the model showed a slight tendency to underestimate (mean normalized bias for 30-day average concentrations over all sites and seasons in the range of 20–40%; Luecken et al. 2006). In MATES-II (2000), annual concentrations of most VOC were within 15% of the measurements at ten sites on average, although some species were significantly underestimated (e.g., 1, 3-butadiene by a factor of 2) or overestimated (e.g., acetaldehyde by a factor of 1.6). Pratt et al. (2004) concluded that their source-specific model simulation results were within a factor of two of the measurements (matched in space and time) on average. Model performance was best for pollutants emitted mostly from mobile sources and poorest for pollutants emitted mostly from area sources. Pratt et al. listed improving the emission inventory (better localization of the sources and better quantification of the emissions) as the best way to improve model performance.

Model performance evaluation was conducted for simulation of a pesticide, atrazine, with a grid-based model (Cooter and Hutzell 2002; Cooter et al. 2002). Performance of grid-based models has not been evaluated for metals, except mercury (which is discussed below for atmospheric deposition). Some evaluations of source-specific models have been conducted for metals (e.g., MATES-II 2000). No direct evaluation has been conducted for diesel particles because of lack of measurements specific to this type of particle. Black carbon has been used as a surrogate in some studies because diesel particles typically contain about 50% of black carbon. However, this approach assumes that no other major sources of black carbon exist (Seigneur et al. 2003).

The treatment of meteorology is also very important to be able to correctly predict air pollutant concentrations in complex flow situations characteristic of neighborhood scale. For example, pollutant concentrations near roadways are particularly sensitive to the vertical dispersion characteristics of the atmosphere (Venkatram et al. 2007) and the presence of noise barriers (Bowker et al. 2007). Air pollutant concentrations in street canyons are difficult to simulate because of the complex air flows rarely measured (Kastner-Klein et al. 2004; Britter and Hanna 2003).

Source Apportionment EPA in its guidelines for the performance evaluation of models for PM and regional haze recommends that receptor models be used to corroborate the results of air quality models. Receptor models use statistical analyses of ambient chemical concentration measurements to estimate the contribution of various source categories to PM concentrations (Hopke 1985; McMurry et al. 2004). They can be used without consideration of air mass transport, or can be combined with back-trajectories analyses of winds to identify the corresponding upwind source areas. One example of the application of receptor modeling techniques to corroborate the results of air quality models is the Big Bend Regional Aerosol and Visibility Observational (BRAVO) study. The BRAVO study addressed the contribution of U.S. and Mexican source areas to sulfate concentrations in Big Bend National Park, Texas. Sulfate is the major contributor to regional haze surrounding Big Bend during summer months. After reconciliation of the modeling results and correction for model bias, the air quality models and receptor models led to similar relative contributions of the Mexico, Texas, eastern U.S. and western U.S. source areas to sulfate concentrations around Big Bend, thereby providing confidence in the predicted source area contributions (Schichtel et al. 2005). Both air quality models and receptor models have pros and cons and their combined use helps improve our understanding of source contributions. For example, Marmur et al. (2006) showed that for $PM_{2.5}$ in the southeastern United States air quality models lack temporal representativeness (because of limited temporal information in emission inventories) whereas a receptor model such as the Chemical Mass Balance (CMB) lacks spatial representativeness (unless a dense speciation monitoring network is available). Another example of receptor modeling is the source apportionment of VOC in Mexico City (Vega et al. 2000; Mugica et al. 2002; Wöhrnschimmel et al. 2006).

Perhaps the best applications of receptor modeling have been obtained for source apportionment of PM_{10} in cases where the secondary fraction is a minor component. Although receptor modeling techniques are based on ambient monitoring data, many uncertainties are associated with their use and caution is advised when interpreting their results. Engel-Cox and Weber (2007) present a summary of recent applications of two receptor modeling techniques based on factor analysis; Reff et al. (2007) present a discussion of one quantitative method based on factor analysis (the Positive Matrix Factorization) and highlight the sensitivity of the results to the choice of the method parameters (species selected in the analysis, number of factors, etc.). Watson et al. (2008) provide an overview of recent receptor modeling applications in the context of the EPA Supersite Program. Lee et al. (2008) offer a critical comparison of two standard receptor modeling techniques (Chemical Mass Balance and Positive Matrix Factorization) and discuss their limitations. One of the more critical of these is the lack of capability to directly assign sources for secondary particles.

Dynamic Evaluation The prediction of the response of ambient concentrations to changes in emissions can be challenging because of the non-linearity of secondary pollutant formation pathways. Figure 9.5 depicts the response of $PM_{2.5}$ components to 50% changes in precursor emissions for a summer episode in the southeastern United States; some of those responses are complex and non-intuitive. Pun et al.

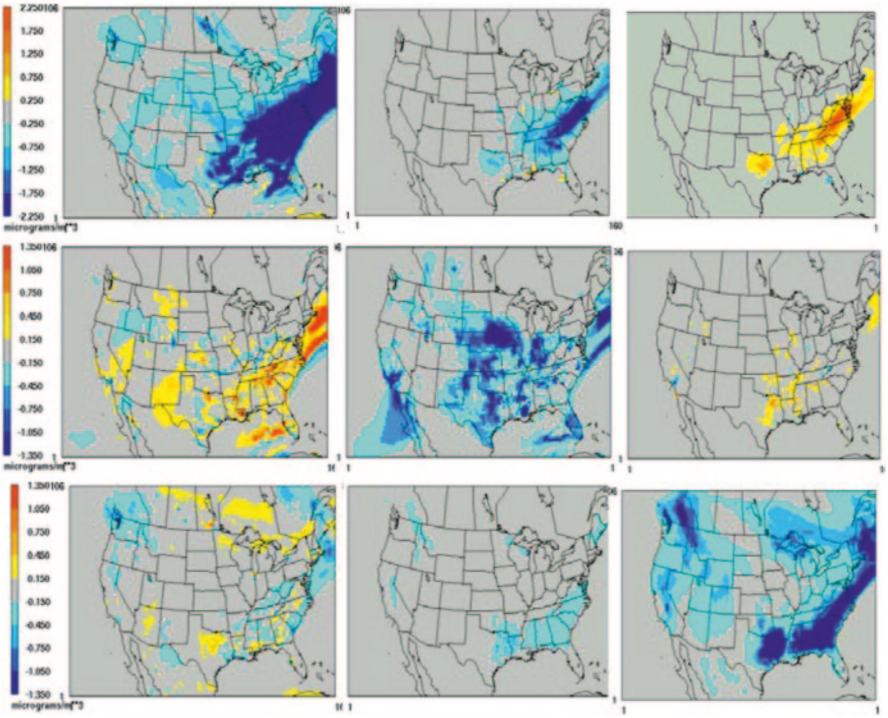


Fig. 9.5 Response of the Concentrations of $PM_{2.5}$ Components of Sulfate (*top row*), Nitrate (*middle row*) and Organics (*bottom row*) to 50 % Reductions in SO_2 (*left column*), NO_x (*middle column*) and VOC (*right column*) Emissions Simulated over the Contiguous United States for the 1–10 July 1999 period. (Source: Seigneur 2005)

(2007) showed that poor operational performance is very likely to lead to a poor ability to predict model response to emission changes. However, satisfactory operational model performance does not necessarily guarantee that an air quality model will predict the correct response to an emission change. To evaluate model skill, it is necessary to conduct a dynamic evaluation where the model is evaluated for at least two different emission scenarios. Gilliland et al. (2008) conducted such an evaluation for the regional response of ozone concentrations to changes in NO_x emissions in the northeastern United States (see also Godowitch et al. 2008). Such dynamic evaluations require detailed emission inventories for the years of interest. Differences in emissions between weekdays and weekends can also be used to that end. For example, Yarwood et al. (2003) showed that an air quality model could reproduce the day-of-the-week variability of ozone concentrations in the Los Angeles Basin.

Another approach to evaluating the ability of models to predict the response to emission changes is using measurements of chemical species that provide information on the chemical regime of the atmosphere (e.g., NO_x vs. VOC sensitive for ozone, HNO_3 vs. NH_3 sensitive for ammonium nitrate; see McMurry et al. 2004; Pinder et al. 2008 for more details).

9.1.4 Areas for Future Improvement

Areas for future improvement in air quality modeling as applied to population exposure and health effects studies, for advancing to *Levels 3* and *4*, include all areas where the current needs of the exposure and health communities are not met by existing air quality models.

Spatial Resolution A major area for improvement is the representation of the sharp concentration gradients that occur near emission sources, mostly near roadways as population exposure is very sensitive to those spatial concentration gradients (Jerrett et al. 2005). Some modeling techniques were described above that approach this problem. Each of those techniques needs to be evaluated against ambient data to assess their accuracy, to compare those techniques using a common data set to determine their relative strengths and weaknesses, and to further develop the most promising techniques.

Temporal Extent, Trends and Accountability Meteorological and air quality model simulations should be conducted over multi-year periods given the appropriate inputs. The availability of emission inventories is the limiting factor at the moment, because a North American emission inventory that covers a multi-year period with a consistent methodology for emission estimates does not exist and is unlikely to become available in the near future. Clearly, such emission inventories are needed if one wants to apply models to analyze or interpret trends in air pollutant concentrations and to check the effect of an emission changes on air quality over a period of several years.

Chemical Species and Particle Size Air quality models need to be improved for some aspects of their treatment of criteria pollutants. For example, the simulation of photochemical production using new in situ measurements of free radicals needs to be assessed. Considerable uncertainties remain in the simulation of primary gaseous pollutants such as CO, NO_2 and VOC species, as well as in the simulation of primary and secondary organic aerosols. PM characteristics are of interest to the health community and are not currently well treated by air quality models. These are formulated to address air quality regulations rather than multipollutant health research topics. Some air toxics of interest for exposure and health effects studies are not treated in standard air quality models (major VOCs are now treated explicitly but most trace metals are not). Following their improvements, air quality models need to be evaluated against ambient measurements; in many cases these measurements are not available to be compatible with modeling requirements. To the extent possible, diagnostic (e.g., by process, region, and season) and dynamic evaluations will need to be performed.

Emissions Emission inputs are essential for air quality simulations. In particular, the uncertainties associated with emissions typically dominate the uncertainties associated with the simulation results of source-specific models (Sax and Isakov 2003; Hanna et al. 2007). As finer spatial and temporal resolution becomes critical for exposure assessments, the need for reliable emission inventories at finer spatial and temporal scales will increase. There obviously is a practical limit to acquisition of emission information, but it is not known what this limit is.

Meteorology Obtaining more accurate predictions of pollutant concentrations at finer spatial resolution in urban areas implies obtaining reliable meteorological fields (winds and turbulence) within areas with complex building settings (e.g., street canyons; noise barriers near roadways). Meteorological models need to be developed and evaluated to address such complex situations. Some initial efforts are underway in the United States (e.g., Otte et al. 2004) and in Mexico. UNAM-CCA is implementing, in collaboration with San Jose State University, an urbanized version of MM5 that will allow 500-m resolution; finer temporal resolution may be desirable as the spatial resolution increases.

9.2 Atmospheric Modeling for Ecosystem Management

9.2.1 Needs from Ecosystem Modeling

Ecosystem models obtain inputs of atmospheric stressors in terms of air concentrations or deposition load to calculate changes in ecosystem processes, structure, and/or function. (Ecosystem models are described in Chap. 6.) The current models are generally suitable for calculations for *Level 1* and *2* approaches. For *Level 3* and *4*, ecosystem exposure models may require further advancement to account for multipollutant interactions including cation–anion balances, and bidirectional flux calculations. Calculation of atmospheric deposition of chemical species to ecosystems requires knowledge of deposition fluxes of atmospheric chemical species to the Earth's surface. Wet deposition processes include the removal of chemical species from the atmosphere by precipitation (rain, snow, etc.), settling of fog droplets, and impaction of cloud hydrometeors. Dry deposition processes include the removal of chemical species from the atmosphere as they adsorb to, absorb into or react with surfaces such as soil, water, vegetation or man-made structures. Atmospheric species contact surfaces following two major transport steps: (1) turbulent transport, which brings gaseous species or particles near the surface and (2) molecular or Brownian diffusion within the thin air layer that is in contact with the surface. Both wet and dry deposition fluxes are needed as input to ecosystem models. The needs of ecosystem modelers may be further categorized as follows.

Spatial Resolution The spatial resolution provided by an air quality model must be compatible with the spatial variability of the atmospheric fluxes to the ecosystem of interest. Atmospheric fluxes may vary because of changes in air pollutant concentrations (e.g., near a source), precipitation patterns (precipitation may vary significantly with location in mountainous and coastal areas) and land use patterns (which affect dry deposition). Ecosystem models are not constrained to rectangular grids and most follow land use, terrain and the boundaries of water bodies using a grid of irregular polygons. The polygons are typically designed to resolve subcomponents of watersheds. Explicit recognition of different land use types includes water bodies and topography.

Temporal Resolution The temporal resolution needed for atmospheric fluxes to ecosystems is highly variable, from daily to annual, to match ecosystem time scales. For stream chemistry models, current temporal resolution required of the atmospheric fluxes is monthly. The required resolution is expected to increase to daily in the future. For rivers and estuaries, the simpler models operate with annual to monthly time steps, but the more refined, process-oriented models operate with a daily to hourly time steps to treat tidal influences. Providing a daily budget of accumulated dry fluxes is most important. A fine temporal resolution to resolve the diurnal pattern of the atmospheric flux is not required at this time, but could be in the future. At a minimum, seasonal or monthly variations must be provided as the ecosystem will govern the evolution of chemical species differently as the ambient conditions vary (e.g., surface temperature, soil moisture).

Temporal Extent Ecosystems typically react over long time scales, and sulfur, nitrogen, and mercury have a legacy effect. Therefore, soil chemistry, surface water chemistry and mercury models spin up for about 100 years, starting about 1850–1900. The spin up period, until contemporary data are encountered, uses annual time steps and fairly rough estimates of wet and dry deposition, temperature and rainfall. For contemporary data, around 1980–1990 onward, ecosystem modelers prefer monthly deposition data. Some watershed and estuarine models only calibrate against contemporary chemical, hydrologic and temperature data. They may use 5–20 years as a calibration period, because precipitation (hydrology) may vary significantly from year to year. For these models it is important to obtain atmospheric fluxes over several years to capture the inter-annual temporal variability of precipitation patterns, and there is a preference for the atmospheric flux inputs to be monthly or daily. For some models, climatological atmospheric fluxes are acceptable as long as no significant changes in air emissions occur during the period being averaged. Long-term projections into the future tend not to consider changes in meteorology and, hence, repeat a multi-year contemporary period. Thus, there is little accounting for the impact of climate change on the chemical and physical input variables.

Accuracy Because water chemistry models are typically calibrated or spun up against a time series of inputs, high accuracy of the inputs is desirable. Ecosystem modelers would prefer the input accuracy supplied by atmospheric models be on the order of the analytical accuracy of the watershed observations used for inputs. Thus, the lack of accuracy between modeled meteorology and observed hydrology is of concern. A related concern is the incompatibilities introduced in the transition from measurements for hindcasts to atmospheric model predictions for forecasts and a concern about lack of cross-consistency when data come from different sources of measurements and models.

Chemical and Physical Variables The chemical species of most interest to the ecosystem community include ozone; the acidic species (mostly, sulfate and nitrate, but also sulfur dioxide and ammonia [ammonium]) plus the neutralizing species for the more advanced water chemistry models (calcium, magnesium, sodium, potassium, and chloride), which can lead to acidification of water bodies; nitrogenous species (nitrogen oxides, nitric and nitrous acids, organic nitrogen, ammonia, particulate ammonium and nitrate, etc.), which can lead to lake, bay and estuary eutrophication; mercury species (divalent gaseous mercury, elemental gaseous mercury and particulate mercury), which can be methylated in water bodies and lead to high concentrations of methylmercury in aquatic biota via bioaccumulation. Persistent organic pollutants are of interest, as they can bioaccumulate in the food chain, as discussed in Chap. 6. Ecosystem models also require meteorological variables, including temperature, precipitation and photosynthesizing radiation.

Atmosphere/Ecosystem Interface Some chemical species deposit from the atmosphere to surfaces irreversibly; that is, they are not transferred back to the atmosphere. This is the case, for example, for sulfate. Other species may be emitted back to the atmosphere either in their original form or in a different oxidation state. For example, nitrogenous species may be emitted back to the atmosphere as nitric oxide or ammonia, and mercury species may be emitted back to the atmosphere as elemental mercury. Such processes need to be simulated via an interface that accounts for deposition from the atmosphere to an ecosystem, the possible chemical transformation in the ecosystem (e.g., vegetation, top soil layer, wetland or water column), and the emission of some chemical species back to the atmosphere. The atmospheric fluxes to different land use types within a grid cell also need to be associated with the corresponding land use types within the spatial polygons used by the ecological model.

9.2.2 Needs from Ecosystem Critical Load Analysis

The critical load concept is an effect-based approach that attempts to estimate the pollutant concentration level or atmospheric deposition load that would be likely to cause environmental harm (see also Chap. 6). A critical load is specifically defined as a quantitative estimate of an exposure (concentration level or atmospheric deposition) to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment or on ecosystem structure and function do not occur according to present knowledge. A sensitive element can constitute a part of, or the whole of an ecosystem. While it is deposition or air concentration itself that is of interest, the needs of critical load assessments similarly may be categorized as above.

Spatial Resolution Critical loads are directly related to atmospheric fluxes to local/regional natural ecosystems. Critical load values may vary considerably between different ecological zones of North America. Critical load mapping is now being performed at high resolution (30 m to a few km) across North America. The spatial variation of atmospheric deposition to underlying soils and vegetation types and vegetation/soil/bedrock gradients determine the degree of sensitivity of ecosystem functioning. Therefore, critical loads are defined at a high spatial resolution and may be highly variable spatially. The spatial resolution of an air quality model must address variations in atmospheric fluxes due to changes in air pollutant concentrations (resulting from topography), precipitation patterns (precipitation may vary significantly with location in mountainous and coastal areas) and land use and soil patterns (affecting estimation of dry deposition). The air quality model should also be able to distinguish fluxes to different land use types within a grid.

Temporal Resolution Dynamic and steady state ecosystem models are used to calculate a critical load associated with a particular degree of ecosystem protection. These models typically calculate a critical load at a scale of an average annual deposition many decades into the future. Thus, a fine temporal resolution, such as hourly inputs, is not required for projections of future atmospheric fluxes. However, these models may have the same temporal requirements for historical and contemporary flux inputs as those listed in Sect. 9.2.1 for purposes of calibration.

Accuracy Different from the NAAQS, critical loads require chemical components of the atmospheric loading to be measured and combined (e.g., total sulfur and total nitrogen), creating a more complicated set of accuracy expectations to support the use of critical loads to protect ecosystems. The latter also affect critical loading in terms of media chemistry and vulnerability.

Temporal Extent For critical loads modeling using steady state models, the temporal extent involves multi-year averages to smooth out inter-annual meteorological and deposition variability. For critical load calculations using dynamic models, it is desirable to provide deposition simulations spanning multiple years to account for emission changes as well as inter-annual variability. For both types of models, long-term projections and, potentially, an accounting for the impact of climate change on the input variables may be needed. Emission projections are essential for estimating long term effects. This is a particularly challenging aspect of studies of atmospheric-ecological stress.

Chemical Species The chemical species of most interest to the critical loads community at this time include: ozone and the combined effects of total sulfur (sulfate and sulfur dioxide), total nitrogen, (oxidized and reduced inorganic nitrogen and dissolved organic nitrogen) and mercury. Ozone affects vegetation on direct contact. Deposition of the combined acidic sulfur and nitrogen species can lead to acidification of soils and vulnerable water bodies and the release of aluminum (an important causal agent of ecosystem damage and degradation), as discussed in Chap. 6.

Atmosphere/Ecosystem Interface The atmospheric fluxes to different land use and vegetation types within a grid cell need to be linked to the parallel land use types within the polygons used by critical load mapping. Addressing the potential bi-directionality of the atmospheric flux in the air-surface interface may be less important for natural systems than for anthropogenically impacted systems, such as agricultural practices. However, the transport of pollutants to natural systems will be affected by bi-directional fluxes occurring in the intervening landscape.

9.2.3 Current Status of Atmospheric Deposition Models

Current deposition models calculate the wet and dry deposition fluxes of several major chemical species. Calculation of wet deposition fluxes requires knowledge of the concentrations of the species of interest within the cloud droplets, raindrops, snowflakes, ice crystals and fog droplets, as well as the precipitation rate (see Fig. 9.6 as an example of precipitation and wet deposition of sulfate, nitrate and ammonium simulated over Canada and the United States with the Environment Canada model AURAMS). Calculation of dry deposition fluxes requires knowledge of the atmospheric characteristics (turbulence, temperature), chemical species properties (molecular or Brownian diffusion coefficient, ability to adsorb, absorb or

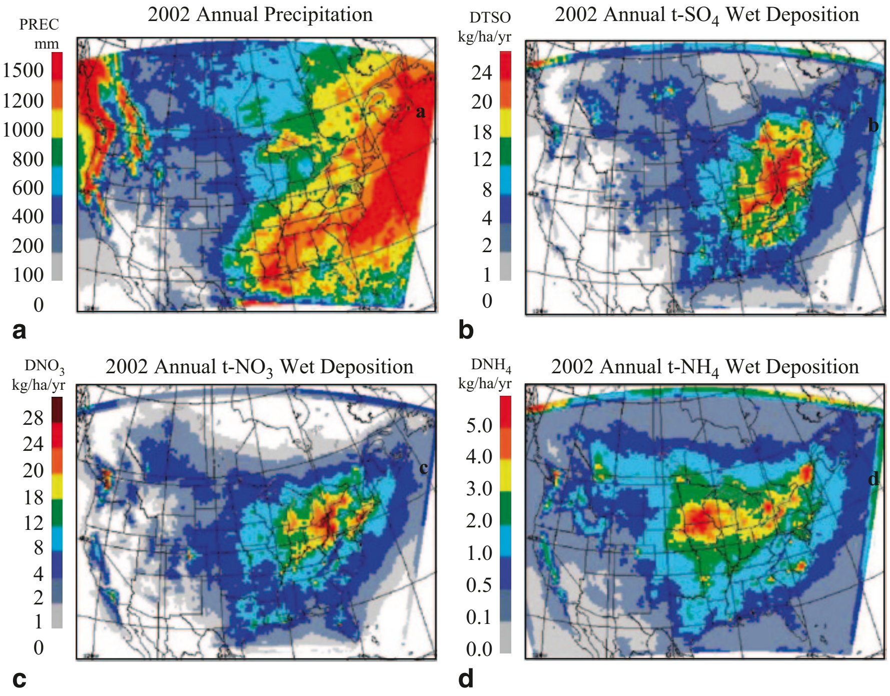


Fig. 9.6 Simulation of (**a**) annual precipitation (mm), (**b**) sulfate, (**c**) nitrate, and (**d**) ammonium wet deposition fluxes (kg $ha^{-1}y^{-1}$) over Canada and the United States for 2002 with the Environment Canada Chemical Transport Model AURAMS. (Source: Moran et al. 2008)

react) and surface properties (ability to retain gaseous species). We discuss below whether current atmospheric models are suitable to address the specific needs of the ecosystem modelers.

Spatial Resolution Regional models calculate atmospheric deposition fluxes on a rectangular-type horizontal grid. The most common geographical projections are Lambert conformal, Universal Transverse Mercator, and latitude-longitude, with a spatial resolution that ranges from a few kilometers to several tens of kilometers. Therefore, the gridded atmospheric deposition fluxes may not correspond to the areas relevant to the ecosystem model. For example, a given grid cell may cover a combination of some land areas and some water areas. Thus, the atmospheric flux calculated by the model represents an average over a mixture of water and land areas within the grid, and may differ from both the atmospheric fluxes to the water area and to the land area. Furthermore, the land area may include different land use types (e.g., bare soil, vegetation) that may lead to significantly different atmospheric dry deposition fluxes. For example, the mercury deposition flux is significantly greater to a deciduous forest than to bare soil (Lindberg and Stratton 1998). Also, topographic effects in complex terrain are not well represented at current grid resolutions.

Temporal Resolution The temporal resolution provided by air quality models is one hour because meteorological and emission inputs are typically available on an hourly basis. This resolution is much finer than needed for input to ecosystem models and is, therefore, quite sufficient.

Temporal Extent, Trends and Accountability Air quality model simulations are now routinely conducted for one-year periods. However, there are very few examples of multi-year air quality simulations at regional scales, and none yet in which all emissions are truly varied by year of interest. Such multi-year simulations require geographically specific emission inventories for each year of a simulation period. To date, emission inventories have only been available for a given year of interest. These are available every few years but with changes in methodology (see Chap. 8), which has limited the possibility of multi-year simulations. Modeling tools are available for the development of emission inventories for future years (prospective modeling); however, significant effort is required to develop such inventories, particularly in terms of data collection. Moreover, the application of modeling tools for the development of emission inventories for past years is limited by the availability of pertinent data. The need for multi-year emission inventories that are internally consistent in terms of methodology was identified by NARSTO (2005). EPA is currently setting up such an approach. Once those multi-year emission inventories become available, multi-year air quality simulations that account for emission changes will be feasible.

Accuracy The meteorological variables are provided by the meteorological models, such as temperature and precipitation, may differ significantly from actual values available from local measurements. Current models, for example, do not provide sufficiently precise estimates of precipitation and chemical deposition, and therefore are not used in water chemistry/hydrology model calibration. Observed precipitation and deposition with some type of spatial interpolation is used instead. This leads to some inconsistencies in addressing the effects of change in deposition loading between current conditions (measurement determined) and future (calculated from meteorological/air quality models).

Chemical and Physical Variables Air quality models currently calculate deposition of ozone (see Fig. 9.7 for deposition of ozone over the continental United States simulated with the CMAQ model), sulfate, sulfur dioxide, oxidized-nitrogen and reduced-nitrogen compounds (see Fig. 9.8 for total deposition of oxidized-and reduced-nitrogen over the continental United States simulated with the CMAQ model), and mercury. Two important categories relevant to acidification and critical loads that are not treated are deposition of base cations and deposition of dissolved organic nitrogen (DON). Another major category of chemical species relevant to atmospheric deposition, which is not currently treated by air quality models, is organic toxins listed in Chap. 6, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated biphenyls, dioxins, furans, some pesticides, and chlorophenols; this group of chemicals is generally referred to as POPs. POPs have been modeled mostly in North America using multi-media compartmental models that include major assumptions on the spatial resolution of concentrations (i.e., the atmosphere is often represented by a single well-mixed compartment). Limited attempts have been made to treat POPs in air quality models in North America. The simulation of POPs by air quality models is limited at the moment by (a) the availability of reliable emission inventories (Breivik et al. 2003) and (b) knowledge of their atmospheric chemistry (Franklin et al. 2000).

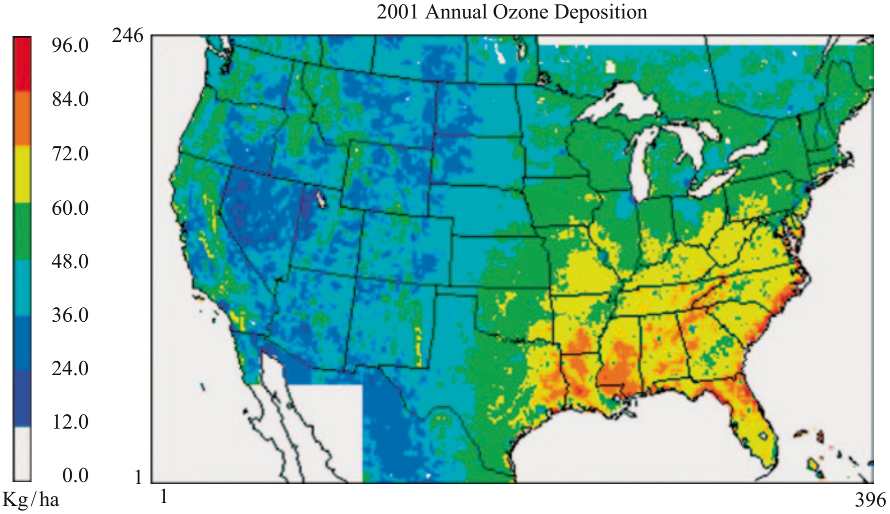
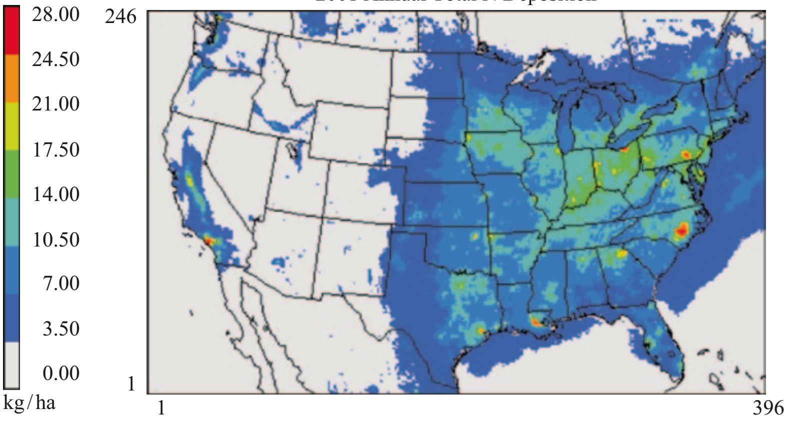
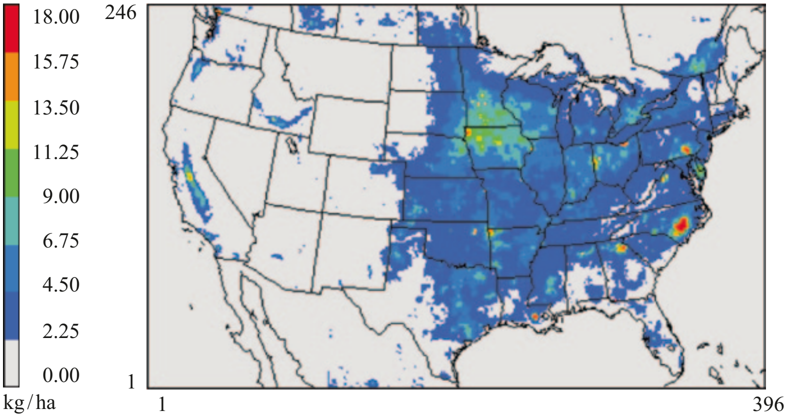


Fig. 9.7 Total wet + dry ozone deposition simulated for 2001 emissions over the continental United States with CMAQ. The total deposition of ozone is essentially all dry deposition


2001 Annual Total N Deposition


2001 Annual Total Reduced N Deposition

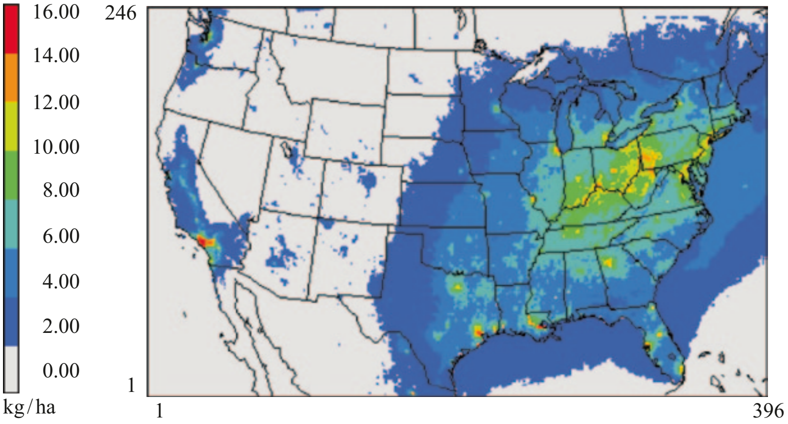

2001 Annual Total Oxidized-N Deposition

Fig. 9.8 Total wet + dry nitrogen deposition simulated for 2001 emissions over the continental United States with the CMAQ. The influence of power plants and transportation corridors is evident in the oxidized-nitrogen deposition pattern, and the influence of confined animal feeding operations is evident in the reduced-nitrogen deposition pattern

Meteorological variables needed by ecosystem models (temperature, precipitation and photosynthesizing radiation) are provided by meteorological models; however, these may differ significantly from actual values available from local measurements, particularly in the case of precipitation. This potential discrepancy raises the question of how to integrate different sources of chemical and physical information (model calibration, data assimilation, data fusion, etc.; see Text Box 9.1).

Text Box 9.1 Elements of Model Calibration

Model calibration consists in the adjustment of model inputs or model parameters/algorithms to obtain better operational performance. *Data assimilation* forces the air quality model predictions toward observations using various mathematical techniques such as a variational analysis, a sequential analysis (e.g., Kalman filter) or an additional "nudging" term in the model equations; although this is now done routinely in meteorology to assimilate wind and temperature observations, the assimilation of air quality observations in air quality modeling has been limited to date (e.g., Chai et al. 2006, 2007). *Data fusion* combines the results of an air quality simulation with data to develop fields of air concentrations or atmospheric deposition fluxes that leverage the best aspects of model results and data; standard interpolation techniques, kriging techniques and hierarchical Bayesian approaches have been used for data fusion (e.g., Fuentes and Raftery 2005). Data assimilation is a dynamic process because the data affect the model simulation as it progresses (on-line procedure), whereas data fusion can be seen as a static assimilation process because the assimilation step does not feed back into the model simulation (post-processing step). Note that in the case of both data assimilation and data fusion, the result is a combination of the model and observations, therefore, it does not correspond to a solution of the original model. Also, these techniques focus on creating a better representation of current conditions.

Atmosphere/Ecosystem Interface Most air quality models do not currently account for the possible transformation of chemical species in an ecosystem and the emission of derivative species back to the atmosphere. Some interfacial algorithms have been developed for mercury (e.g., Lin et al. 2005), but they have not yet been incorporated into standard air quality models. Most air quality models do not yet treat the bi-directional exchange of nitrogenous species, controlled by chemical and physical conditions at the plant/soil level, especially ammonia. But some algorithms are being developed for North American conditions at NOAA/EPA.

9.2.4 Evaluation of Atmospheric Deposition Models

Air quality models are evaluated for ambient concentrations, wet deposition fluxes and, in rare cases, total or dry deposition fluxes. As discussed above, an operational evaluation is not sufficient to guarantee the ability of an air quality model to quantitatively predict the response of atmospheric deposition fluxes to changes in emissions. Source apportionment and dynamic evaluations are, therefore, recommended to complement the operational evaluation. We summarize the current status of air quality model operational performance for major chemical species.

Ozone Measurements of hourly ozone ambient concentrations near the surface are conducted in remote areas by the Clean Air Status and Trends Network (CASTNET) at 80 sites in the United States and in urban areas by various federal and state networks integrated into the Air Quality System (AQS) database. Model performance for ozone concentrations has been evaluated for regional scales over the contiguous United States (Eder and Yu 2006; Appel et al. 2007), and was found overall to be commensurate with model performance at urban scales (see Sect. 9.2.3), though models with coarse grid spacing (>10 km) have difficulties reproducing urban ozone concentrations in areas with complex meteorology (e.g., Los Angeles basin) and steep emission gradients.

Acid Deposition The National Atmospheric Deposition Network (NADP) and CAPMoN provide weekly measurements of the wet deposition fluxes of sulfate, nitrate, chloride, ammonium, other base cations (calcium, magnesium, potassium and sodium) and hydrogen ions at over 250 sites in the United States and a number of sites in Canada. The Atmospheric Integrated Research Monitoring Network (AIRMoN) provides similar measurements, but with finer temporal resolution (daily), at seven eastern sites. CASTNET provides weekly measurements of ambient surface concentrations of sulfur dioxide, particulate sulfate, nitric acid, particulate nitrate, and particulate ammonium. The ambient concentrations are then combined with estimates of dry deposition velocities to obtain estimates of dry deposition fluxes. The evaluation of wet deposition fluxes for sulfate, nitrate and ammonium have shown that model performance is satisfactory for sulfate (Dennis et al. 1990) but larger uncertainties are associated with nitrate and ammonium (Mathur and Dennis 2003). Nitrate fluxes are reasonable for the cold season but are biased low in the warm season. Evaluation of ammonium fluxes has been tied to inverse modeling to establish estimates of ammonia emission seasonality (Gilliland et al. 2006).

Uncertainties in wet deposition fluxes are compounded by errors in local precipitation predictions of the meteorological models. There continues to be significant spatial variability in errors even when the regional deposition pattern is relatively unbiased. The evaluation of dry deposition fluxes with routine network data is not a direct evaluation because (a) the deposition velocity is estimated for the measurement network using meteorological data taken in cleared areas which are generally not representative of deposition in varied land use, and (b) the dry deposition velocity differs from that calculated by the air quality model, in part, because the parameterization used to infer dry deposition from observed data differs from the dry deposition algorithm imbedded in the air quality model. Furthermore, the measurements of gaseous nitric acid, particulate nitrate, and particulate ammonium are approximate because of sampling artifacts and, in addition, gaseous ammonia data are generally missing.

Nitrogenous Compounds Atmospheric deposition of nitrogenous compounds encompasses a large number of nitrogen-containing species; however, a few of these species tend to dominate the nitrogen deposition budget. Typically, nitric acid (and its associated particulate nitrate), ammonia (and its associated particulate ammonium) dominate in rural areas, with nitrogen oxides (NO and NO_2) and organic nitrates contributing less but significantly. Therefore, the evaluation of inorganic nitrate and ammonia/ammonium for acid deposition is directly pertinent to the evaluation of models for the atmospheric deposition of nitrogenous compounds since it covers the largest fraction of the nitrogen deposition budget.

Mercury The Mercury Deposition Network (MDN) measures the wet deposition flux of mercury species on a weekly basis at over 90 sites in the United States and Canada. No North America-wide network measures either ambient concentrations of the major mercury species groups (i.e., elemental mercury, gaseous oxidized mercury and particulate mercury) or the dry deposition of mercury, although there have been some proposals to establish such a network in the United States (Lyman et al. 2007) with success for ambient concentration measurements. The Southeastern Aerosol Research and Characterization study (SEARCH) includes several stations in the southeastern United States that measure ambient concentrations of speciated mercury and mercury wet deposition. Model performance for mercury deposition depends significantly on the model formulation, simulated precipitation fields and boundary conditions (because mercury is a global pollutant). The evaluation of mercury wet deposition is conducted routinely using the MDN data; recent results have shown differences among models due to, in order of decreasing importance, model formulation, boundary conditions, and simulated precipitation (Bullock et al. 2009). As there are currently no dry deposition data for model evaluation, models have been evaluated instead using the few mercury speciated concentrations available. Although models tend to reproduce the global-scale gradients in total mercury concentrations and elemental mercury concentrations (most atmospheric mercury is elemental; e.g., Selin et al. 2007; Lohman et al. 2008), model performance for gaseous and particulate divalent mercury is more variable due to the shorter lifetime of those species in the atmosphere and the interactions between gaseous divalent mercury species and particulate matter (e.g., Seigneur et al. 2004; Selin et al. 2007).

Source Apportionment and Dynamic Evaluations The ability of an air quality model to properly attribute atmospheric deposition fluxes to various source categories and/or upwind source areas should be investigated. As for ambient concentrations, receptor modeling techniques can be used to that end. Dynamic evaluations would also be necessary to complement source apportionment evaluations for cases where the atmospheric deposition/precursor emission relationship is non-linear (e.g., nitrogen deposition). In the case of nitrogen deposition, a possible option is the use of nitrogen isotopes in wet deposition (Elliott et al. 2007). As another example, Keeler et al. (2006) applied two receptor modeling techniques (Positive Matrix Factorization, PMF, and UNMIX) to wet deposition data collected at Steubenville, OH, to estimate the relative contribution of coal combustion sources to mercury wet deposition, which was 70 ± 15%. A chemical transport model for atmospheric mercury (Seigneur et al. 2004) estimated a contribution of U.S. coal-fired power plants (a subset of coal combustion sources) to mercury deposition in the Steubenville area of 62%, i.e., a value well within the range of 55–85% obtained with the receptor modeling techniques. (Note: This community is in an area where many large coal-fired power plants are located.)

9.2.5 Areas for Future Improvement

Several improvements of atmospheric models and their interface with ecosystem models can lead to significant advances in our ability to provide the needed inputs to ecosystem models.

Spatial Resolution It is desirable to calculate dry deposition fluxes at a scale compatible with that of the ecosystem model using sub-grid scale land use information for dry deposition fluxes. It is also desirable to improve the meteorological model parameterizations to provide better quality precipitation estimates at spatial scales down to 1 km and terrain effects on air concentrations and dry deposition fluxes at grid sizes of 1–4 km.

Accuracy It is desirable to reduce the error in precipitation simulations and air-surface flux estimates for daily to monthly temporal averages to provide more accurate data that can be input to the water quality models, potentially as data for accountability analyses. The adaptation of chemical data assimilation techniques or development of methods to combine measured and modeled data (data fusion) are worth investigating to help reduce error in the precipitation and deposition fields and reduce disparities with calibration data.

Temporal Extent, Trends and Accountability Development of a consistent, continuous time series of physical parameters (especially temperature and precipitation amount) and air-surface flux from the meteorological and chemical transport models is becoming a necessity for trend analysis. For practical purposes, this series could effectively start around 2001 which marks the beginning of the period for which consistent methodologies for estimating emissions across multiple years, from sources other than power plants, are being developed and when NO_x emissions begin to change noticeably. Meteorological and air quality model simulations could be conducted over multi-year periods given the appropriate inputs and compared with measurements (see, e.g., Chap. 12). The availability of emission inventories is the limiting factor at the moment. A continuous, historical time series of physical parameters and air-surface flux, starting around 1900, could be developed for the ecosystem models as collaboration between the air quality and ecosystem modeling communities. Such a historical time series needs to smoothly transition to current empirically-based and model-based time series. Looking to the future, guidance on the inclusion of climate change impacts on hydrology and chemistry for long-term projections of deposition (50 years in the future) needs to be developed.

Chemical Species The major chemical species of interest for atmospheric deposition are simulated routinely by atmospheric models (i.e., ozone, sulfate, nitrate, ammonium, other nitrogenous compounds with the exception of dissolved organic nitrogen (DON), and mercury). But there are still significant uncertainties in our ability to correctly simulate the atmospheric deposition of nitrogenous compounds and mercury, and we lack the necessary information (emissions inventories and model formulations) to simulate DON. However, base cation assimilation is needed by the more advanced soil and surface water chemistry models and base cations are not simulated by current atmospheric models; there is enormous uncertainty regarding emissions that would have to be overcome through inventory development. POPs are not currently treated in most atmospheric models; emission inventories and model representations of their atmospheric fate and transport need to be developed, incorporated into atmospheric models and evaluated with ambient measurements of air concentrations and deposition fluxes.

Atmosphere/Ecosystem Interface Air-surface exchange algorithms in the air quality models need continued evaluation and improvement. These algorithms also need to calculate dry deposition fluxes for specific sub-grid scale land use categories compatible with that of the ecosystem models. Most air quality models do not currently account for the possible transformation of chemical species within an ecosystem and emission of chemical species back to the atmosphere. This is particularly important for nitrogenous species (nitric oxide and ammonia), mercury and POPs. Some interface algorithms have been developed that need to be incorporated and tested in atmospheric models and new algorithms need to be developed, evaluated and incorporated into the models.

9.3 Atmospheric Modeling for Risk Assessment

Risk assessments are conducted to address both human health and ecological impacts as noted in Chap. 4. The issues addressed above are for exposure and health effects studies and for atmospheric deposition to ecosystems. Therefore, they are pertinent to the application of atmospheric models in risk assessment. Guidelines for risk assessment generally require an uncertainty analysis to be conducted in addition to the deterministic analysis for representative individuals or the general population (NRC 1994). Therefore, one aspect of atmospheric modeling that needs to be considered when using atmospheric models in the context of risk assessment is the treatment of uncertainties. There have been limited attempts to account for uncertainties in air quality modeling.

Because taking into account uncertainties requires sampling various values from the probability distribution functions (pdf) of model inputs and parameters, a large number of simulations is generally required. However, grid-based air quality models are computationally demanding and conducting a large number of simulations (e.g., >10,000) may not be feasible. Three major approaches have been used:

The effect of the uncertainties in model inputs and parameters is simulated by conducting a moderate number of simulations (on the order of 100) based on the optimistic assumption that a large number of simulations is not required to cover the full range of uncertainties if the values of the inputs and parameters being sampled are carefully selected (Hanna et al. 2001; Hanna and Davis 2002).

The effect of uncertainties in model inputs and parameters is simulated by conducting a large number of simulations with a simple air quality model, such as a one-dimensional trajectory model, instead of a three-dimensional model (Bergin et al. 1999; Bergin and Milford 2000; Martien et al. 2003).

The effect of uncertainties in model inputs and parameters is simulated by conducting a large number of simulations with a reduced form of the three-dimensional air quality model; i.e., using a response-surface methodology (Seigneur et al. 1999; Lohman et al. 2000; Phillips et al. 2006).

Reduced-form models are versions of the model that reproduce the major characteristics of the model with a computationally simpler version of the model. A standard approach consists in using a response surface model (Box and Wilson 1951). The first step consists in identifying the inputs and parameters that are the most influential for the model output of interest (typically by conducting a sensitivity analysis). Then, the model output is expressed as some mathematical function of those model inputs and parameters. A response-surface model is, therefore, a parameterization of the actual model results, and it may only be valid for the set of conditions under which it was developed. Since process-specific information may not be explicitly included in the response-surface model, one must be aware of the limitations of the response-surface model. The advantage of the response-surface model over the original model is that its simplicity leads to greater computational speed, which is of particular interest for probabilistic analyses that involve a large number of model simulations.

A major component of an uncertainty analysis is to define the probability distribution functions of the influential model inputs and parameters to properly characterize their epistemic uncertainties (i.e., those uncertainties that can be reduced with more information) and aleatory uncertainties (i.e., variability, those uncertainties that originate from natural randomness and cannot be reduced, even with more information).

9.4 Synthesis

9.4.1 Summary of the Current Status of Air Quality Models for Exposure Assessments, Health Effects Studies, and Ecosystem Modeling

We have reviewed the needs of exposure characterization for the health and ecosystem sciences. We have assessed whether current air quality models can address these needs in a satisfactory manner at least within *Level 1* and *2* of regulatory requirements. Our assessment is summarized in terms of what air quality models can do now, what they could do if input data currently missing were to become available, and what they could do after some pertinent model improvements were to be implemented. Except for obtaining accurate precipitation predictions, most improvements are realizable within the next ten years and several are possible in the next few years.

What Atmospheric Models Can Do:

- They treat criteria pollutants, acidic species, nitrogen species, mercury and some other inorganic and organic air toxics; however, there are uncertainties associated with the atmospheric modeling of those pollutants which, to be addressed, will require improvements in some model inputs (in particular, emissions and meteorology) and model formulation (e.g., better understanding of organic PM).
- They provide good temporal resolution (1 h) for the afore-mentioned chemical species, which is suitable for exposure modeling and ecosystem modeling.
- They provide good spatial resolution for atmospheric concentrations of secondary pollutants and deposition (with nested grid and plume-in-grid treatments if needed for finer resolution in urban areas and near point sources, respectively).
- They can be applied for long-term (seasonal to annual) simulations of the afore-mentioned chemical species.
- Models and measurements can be used together to create optimal concentration "surfaces" for air pollutants through data fusion (as a model post-processing step) or data assimilation (as an optimized modeling approach).

What Atmospheric Models Could Do but Input Data Are Currently Missing:

- Multiple year simulations can be conducted but internally consistent multi-year emission inventories are not readily available yet for periods >5 years; there is, however, an ongoing effort at EPA to develop such nationwide emission inventories.
- Air toxic metals are treated in a model such as CMAQ but the corresponding emission inventories are not currently available.
- The lack of compositional information and emission inventories currently precludes the simulation of the deposition of dissolved organic nitrogen.

What Atmospheric Models Could Do but Some Improvements Are Needed:

- Fine spatial resolution for near-source population exposure, in particular, near roadways (the plume-in-grid technology already exists for point sources). Various techniques are currently under development but more testing and development are needed before they become operational.
- The treatment of several air toxics (e.g., POPs, atmospheric chemistry of hexavalent and trivalent chromium) and some PM characteristics (acidity, ultrafine number) is currently missing in air quality models and the corresponding emission inventories are not available (e.g., ultrafine PM, POPs)
- Two-way surface exchange, which is needed for a correct representation of the atmospheric deposition of nitrogenous and mercury compounds, is not currently

treated in air quality models; some two-way surface exchange modules exist but they need to be incorporated into air quality models and evaluated with experimental field data.

- Enhanced spatial resolution down to 1 km particularly in complex terrain, to account for topographic effects on deposition fluxes and air concentrations.
- The allocation of dry deposition to land-use classes within a model grid is desirable to provide proper dry deposition inputs to ecosystem models; it cannot currently be performed by air quality models, which only provide a grid-average atmospheric deposition flux. There is, however, an ongoing effort to address this issue.
- Models and measurements can, in theory, be used together to create optimal "surfaces" of atmospheric deposition through data fusion; however, discrepancies between modeled and measured precipitation amounts and between dry deposition algorithms need to be resolved satisfactorily before such data fusion techniques can be used routinely. Also, some critical species data are missing for deposition pathways.
- Models do not currently treat the deposition of alkaline species that act to neutralize acid deposition (potassium, calcium, magnesium and sodium). Emission methodologies for those species are currently missing and, as a result, emission inventories are not available (except for sea salt sodium).
- Accurate precipitation estimates are needed at all scales, particularly for the prediction of atmospheric deposition. They also required for PM and regional haze modeling; although there will always be some uncertainty associated with local precipitation fields, some effort must be made to reduce such uncertainties.
- Improvements to models could be checked via diagnostic and dynamic evaluations. Diagnostic evaluations could address individual processes to the extent possible as well as model performance by spatial region and time periods (e.g., by season). Dynamic evaluations (which require robust multi-year emission inventories) are essential to build credibility for the application of air quality models to the design of emission control strategies.

9.4.2 Use of Air Quality Models for Accountability

Air quality models can play an important role in ensuring that emission strategies lead to the desired or projected results. Because they incorporate key chemical and physical processes and potential nonlinear interactions, air quality models can play an important role in explaining and interpreting trends or the lack thereof. Air quality models are ideally suited to separate out the role of meteorology from the role of emissions and chemistry to characterize emissions/exposure relationships or emissions/deposition relationships independently of the meteorological variability (however, the models must first be subject to diagnostic and dynamic evaluations to ensure that they can realistically represent the influence of meteorology and emissions on air pollutant concentrations and deposition fluxes). Air quality models provide more detailed information (spatially, temporally and chemically) than monitoring networks can ever provide in practice. Consequently, air quality models can be used to complement monitoring networks to provide more complete information on the air pollutant concentrations and deposition fluxes and can assist monitoring design, including future designs that take into account anticipated changes in concentrations and/or deposition fluxes. The link between human exposure and ambient concentrations needs to be quantified using parametrization of indoor–outdoor relationships for multipollutants estimated for buildings and vehicles, taking into different geographical climate regimes, building practices and personal activity. These steps are considered a priority to realize regulatory support at *Levels 3* and *4* as discussed in Chap. 3.

Data fusion, where model simulation outputs and measurements are combined to create continuous concentration and deposition fields that are consistent with the available measurements, will be a step in this process. Then, the resulting concentration and deposition fields can be used to track their long-term temporal evolution and to assess whether the changes in emissions over a given time period led to the anticipated changes in atmospheric concentrations and/or atmospheric deposition fluxes. Retrospective analyses of initial modeling calculations of the future need to be designed into major regulatory actions as a feedback mechanism to determine if the projections and their methods were and are reliable.

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Chapter 10
Air Quality Measurements

Richard D. Scheffe, Jeffrey R. Brook and Kenneth L. Demerjian

The goal of this chapter is to address ambient air quality measurements in the context of their current and potential roles for multipollutant air quality management, including accountability assessment. Measurements provide an essential function in support of current air quality management practices and would continue to be critical through all the levels of multipollutant air quality management described in Chap. 3. Current ambient measurement activities vary in scope from long-term monitoring that ensures regulatory compliance to specialized observational programs that support process research. Continuing requirements to serve all these purposes imposes constraints on optimizing measurement activities to address the potential needs of multipollutant management and accountability. However, these future needs must be examined beyond their broad technical elements, to determine how air quality measurement activities would need to be modified to most effectively inform multipollutant management.

Modifications that might be made to current measurement practices will depend on the specific management strategies adopted in Canada, the United States, and Mexico. Several factors that need to be considered in addressing multipollutant requirements at *Levels 1* and *2* (see Chap. 3 for definitions) and beyond have been identified in earlier chapters of this assessment, notably:

1. Stronger integration of the measurement needs of the atmospheric, health, and ecological sciences communities in order to achieve the end-to end accountability envisaged in Figs. 3.1 and 3.2. This will require:
    (a) Linking ambient air concentrations to the actual exposures of individuals, affected populations and targeted ecosystem species.
    (b) Measurements and monitoring to provide data representing multiple scales to serve an increasingly broad user community.
    (c) Increased reliance on models to extend the observations in space and time and to couple them with observations and models that characterize other

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media (soil, water, biological systems, including humans) and relate them to emissions.

2. Ongoing demands for establishing priorities for those measurements that serve statutory obligations regarding single pollutant air quality management objectives.
3. Resource constraints and trade-offs, including staffing and financial support, determine the design and operation of future measurement programs. These can be offset somewhat by the introduction of new, more reliable and potentially more economical instrumentation, but resource constraints will continue to limit the spatial and temporal coverage of observations.

The first steps toward a measurement system that supports multipollutant air quality management will include: (a) determining the strategic needs the measurement scientists must meet in addressing multipollutant goals, (b) auditing the current system for strengths and weaknesses within the chosen strategy, and (c) modifying or redesigning the system to optimize its capabilities to address the designated strategy. Within this framework, there are three questions of particular interest:

1. How effective are current North American monitoring/measurement practices for meeting the diverse needs of today?
2. How might these needs change with application of a multipollutant air quality management approach, including risk analysis and accountability?
3. What practical modifications would effectively support current requirements for air quality management at *Levels 1* and *2* while facilitating transition to *Levels 3* and *4* of multipollutant air quality management, including enhancement of an accountability-based system linking emissions to the desired outcomes of reduced impact on human health and ecosystems?

Principal applications of current measurement systems include:

1. Documentation of ambient concentrations of specific pollutants in urban and rural locations, providing information on how they change in space and time in relation to emission changes or natural phenomena, including meteorological variability.
2. Compliance monitoring associated with specific regulatory goals.
3. Epidemiological research to quantify ambient concentration-response relationships—assuming that human response to pollutant exposure can be inferred by using outdoor concentration (community monitoring) as a surrogate for exposure.
4. Determination of the impacts of atmospheric deposition on aquatic or terrestrial ecosystems.
5. Improving emission, air quality, and multimedia models for retrospective and prospective management applications through comparison and evaluation of the models, and the merging or "fusion" of observations with modeling output.

From an observational perspective, multipollutant air quality management presents challenges related to estimating exposure on the basis of ambient concentrations, composition, and the spatial and temporal structure of pollutants. Given health or ecological response relationships based on exposure, effects can be estimated with increased confidence. Accountability requires added attention to long-term, sustained spatial and temporal scale observations associated with different pollutants relative to emission changes. Accounting for the origins of pollution from many sources from local to regional scale adds a major challenge to account for emission reductions in ambient air quality. Exposure and receptor response derives from the contributions of local, regional and hemispheric to global sources to ambient concentrations. The relative importance of these contributions varies widely across North America depending on the nature of the receptors. A further challenge to observation programs is the need to maintain measurement continuity and sustainability over many years in order to establish the basis for tracking and interpreting changes in emissions to health and ecosystem responses. The breadth and scope of information needs in space and time requires an increased reliance on models to complement and expand observations not only for single pollutant conditions, but also for multipollutant applications.

This chapter is organized to address the three principal questions stated above. The first part provides a summary of current measurement programs across North America (Sect. 10.1 and Appendixes B–G, www.narsto.org). This summary is followed by an assessment of how well current monitoring programs characterize the chemical composition and the spatial and temporal structure of air pollution (Sects. 10.2–10.6). The assessment is conducted in light of the limitations already hindering the scientific and regulatory community in understanding the causes and characteristics of poor air quality, developing effective mitigation policies, and linking trends or lack thereof to results of past policies. Such limitations are likely to pose a greater challenge in the future given the requirements of risk- and results-based multipollutant air quality management. Lastly, Sect. 10.7 discusses the measurement needs for addressing accountability and supporting air quality modeling. Priorities and recommendations for improving current measurement programs and meeting future needs are summarized in Sects. 10.8 and 10.9, with notes on resource constraints.

10.1 Existing Observational Systems

Observational systems supporting air quality and related assessments include routine ground-based regulatory networks, deposition networks, specialized field studies, aircraft-based systems, and to a more limited extent, satellite-based remote sensing platforms. These are supplemented by an extensive meteorological monitoring system, including ground and aloft observations, as well as satellite surveillance. Overviews of North American observation programs have been provided by Demerjian (2000) and Parrish and Fehsenfeld (2000). Details can be found in Appendixes B–G (www.narsto.org). This narrative assumes that readers are familiar with the basic features of existing air quality monitoring programs:

- U.S. networks emphasize regulatory compliance-based measurements, and support many underlying research or strategic studies that form the basis of air quality management within the Clean Air Act. Historically, there has been an abundance of urban and rural sites designed for monitoring surface concentrations of criteria pollutants, but a relative shortage of HAPs measurements as well as aerometric observations aloft.
- Like the U.S. networks, the Canadian measurement program is associated with equivalent compliance concerns and a variety of applications or research-based objectives, resulting in a broad portfolio of routine measurement efforts and special studies. Most measurements have concentrated on southeastern Canada (Great Lakes to the Atlantic), Alberta, and the Vancouver, BC, area. However, the Canadian program also includes sites that cover many of the medium-sized population centers throughout the country as well as important remote sites in the Arctic and elsewhere in support of global atmospheric chemistry research programs.
- Long-term monitoring of air quality in Mexico has taken place mainly in Mexico City, but it has been expanded recently to some large urban areas, as well as U.S.-Mexico border cities (see Text Box 10.1). The observations include the criteria pollutants (CPs) with some intermittent sampling for VOCs.
- Short-term, intensive field campaigns have enhanced the data from basic long-term monitoring with added temporal, compositional and vertically resolved measurements for regulated and non-regulated species of interest in order to improve knowledge of air pollution processes. These campaigns advance our understanding of various physical and chemical processes related to pollutant movement, transformation and removal, and serve as a basis for evaluating and improving emission estimates and air quality models. A long record of field campaigns exists in North America stemming from the 1970s through the present. Some of these have been reviewed by Solomon et al. (2000); others are discussed by McMurry et al. (2004).
- More recently a loosely coordinated international aerometric system of surface, aircraft and ship-based platforms, complemented by satellite surveillance, has emerged that supports improved knowledge of pollutant transport and background concentrations.

Text Box 10.1 Air Monitoring in Mexico

Pollution conditions in Mexico have similarities and important differences compared with conditions in the United States and Canada. These differences have led to major field studies to elucidate the apparent unique conditions in Mexico. A series of intensive field campaigns in Mexico City and some border locations has advanced the knowledge of aspects of ozone and aerosol pollution in these locations (see Doran et al. 1998; Edgerton et al. 1999; Molina et al. 2003, 2007, 2008). The first official Mexican air quality monitoring network began operating in the Mexico City Metropolitan Area (MCMA) in the late 1960s when fourteen monitoring stations were installed to measure TSP and SO_2. In 1985, with technical assistance from EPA, an automatic air monitoring network, known as the *Red Automática de Monitoreo Atmosférico* or the RAMA, was installed by the Mexican federal government. Currently, the routine monitoring network in the MCMA is operated and maintained by the Mexico City Ambient Air Quality Monitoring System (Sistema de Monitoreo Atmosférico de la Ciudad de Mexico, SIMAT) of the Environmental Secretariat of the Federal District. SIMAT provides 49 sites for the measurement of criteria gases, aerosols, and atmospheric deposition, 36 of which are located inside the Federal District (http://www.sma.df.gob.mx/simat/).

On the national level, Mexico is consolidating the monitoring efforts under the National Air Quality Monitoring Program (Programa Nacional de Monitoreo Atmosférico, PNMA) to provide diagnostic and surveillance capability of air quality that enables comparability across different sites and air quality networks and serves as a foundation for the design and establishment of environmental policy. The Program is operated by the National Institute of Ecology (INE) of the Ministry of the Environment (SEMARNAT). The INE also maintains the National Air Quality Information System (SINAICA; http://sinaica.ine.gob.mx/). (See also Appendix B, www.narsto.org.)

10.2 Measurement Network Gaps and Their Implications

10.2.1 Coverage from Present-Day Networks

More than 3,000 air monitoring sites in operation across North America (shown schematically in Fig. 10.1) are equipped to measure for CPs and HAPs (e.g., Appendix B, www.narsto.org). The measurements at any given site include a subset of observations, ranging from one pollutant to multiple pollutants, depending on the purpose of the network. This monitoring system is complemented and supported by ground-based meteorological measurements both in urban and rural sites across the continent, and by upper-level observations at selected locations, using rawinsondes or acoustic sounders. Intermittent, specialized aircraft observations complement the ground-based data. Satellite observations are also available and can be used to supplement, at least qualitatively, ground-based observations, with certain scale limitations. (e.g., Fishman et al. 2008; Hoff and Christopher 2009). Although limited, the aircraft and satellite observations add important aerometric data aloft in selected locations for purposes of analysis and model evaluation.

Long-term continuous monitoring networks in the United States are typified by the urban national and state-local air monitoring systems (NAMS, and SLAMS), the rural U.S. Interagency Monitoring for Protected Environments (IMPROVE), and Clean Air Status and Trends Network (CASTNET) systems (e.g., Demerjian

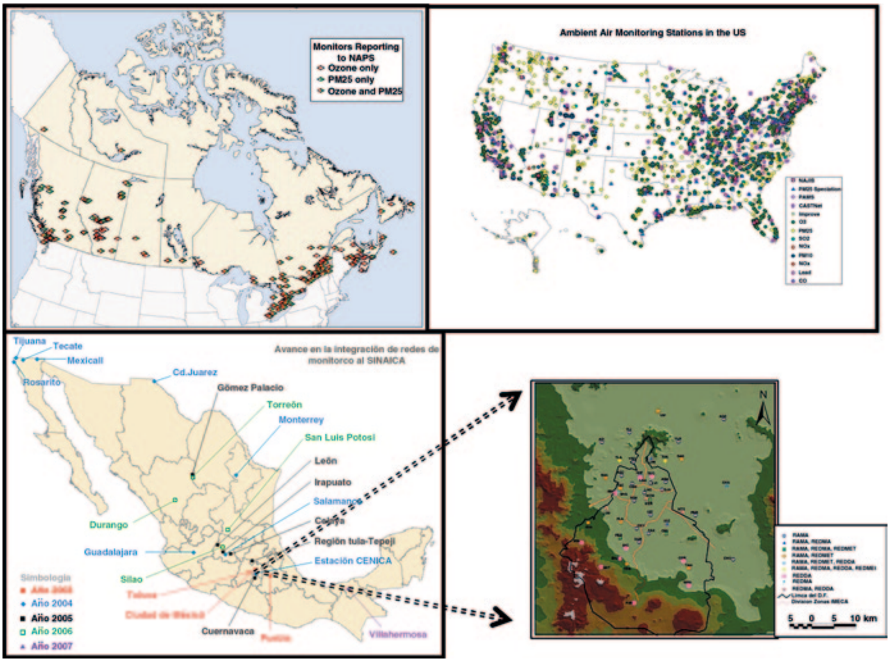

Fig. 10.1 Aggregate map of most of the routine Canadian (*top left*), U.S. (*top right*), and Mexican (*bottom*) monitoring sites, illustrating a broad geographical coverage across North America. The locations represent most of the locations in Appendix B, www.narsto.org. Gaps are seen mainly in unpopulated areas of Canada and Mexico. A significant fraction of Mexican monitoring is located in Mexico City (*bottom right*). The site observations nominally include at least one pollutant; not all pollutants are measured at a given site. The spatial and temporal coverage indicated applies to a subset of measurements at each location. For more details about the networks, see Appendices B and C (www.narsto.org)

2000). In Canada, this type of monitoring is represented by the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the National Air Pollution Surveillance Network (NAPS). Later network deployments in the United States, starting with the Photochemical Assessment Monitoring Stations (PAMS) for VOCs and extending through the PM-speciation (STN), air toxics, and NCore programs, show an evolution toward broadened multipollutant measurement. Other more research-oriented networks (e.g., Southeastern Aerosol Research and Characterization program (SEARCH), CASTNET, the National Acid Deposition Program (NADP), and IMPROVE) incorporate multipollutant measurements at each site.

All of these networks require rigorous quality assurance procedures if their measurements are to be accepted for regulatory or research purposes. Continuous gas or particulate monitoring requires automated data collection, formal quality control procedures, including periodic calibration with reference standards, and recorded data checks. Time-integrated samples (e.g., filters and gas sampling canisters) are transferred from the measurement site to analytical laboratories for analysis. Formal protocols are developed for sample handling and for the variety of analytical procedures required for determining bulk particle composition, VOC speciation and precipitation chemistry. These procedures are quality assured by intercomparisons and the use of common reference standards. On-site chromatography (a typical PAMS analytical method for speciated VOC measurements) and remote-sensing spectroscopy (used in special studies) are capable of identifying a variety of individual compounds, thereby serving as multipollutant sensors. Satellite observations also are capable of adding certain radiation absorbing gases (e.g., NO_2, tropospheric ozone, SO_2, CO and formaldehyde) and aerosol optical depth observations on a large spatial and intermittent time schedule (Hoff and Christopher 2009).

Despite an infrastructure that includes multiple species sensors in many locations, important gaps in key pollutant categories potentially compromise multipollutant air quality management and accountability at *Levels 1* and *2*. These gaps include: (a) insufficient spatial coverage in large cities to evaluate urban gradients in concentrations, or changes in concentrations with demographic changes; (b) limited characterization of airborne particles; (c) unreliable NO_2 or NO_y observations, especially in suburban/rural locations; (d) insufficient spatial coverage of speciated VOC measurements, including biogenic components other than isoprene and oxygenated species, and more spatially limited time-resolved VOC speciation measurements; (e) incomplete speciation measurements of oxidants (e.g., PAN, OH, $NO_3\cdot$, peroxides, and HNO_3); and (f) the absence of observations of ammonia. Additional aerometric measurements of the atmospheric boundary layer including turbulence parameters would also be beneficial for characterizing ground-level conditions with mixing conditions and air mass "aging."

10.2.2 Spatial and Temporal Scale Challenges

In the United States, the multi-agency approach to observational networks has resulted in spatial and temporal coverage beyond that designed specifically for compliance monitoring. However, the linkages between the independently designed networks could be improved. A certain coordination among networks has been achieved through comparison of methods, instrumentation and quality control and assurance procedures to insure consistency in the data obtained. However, an overall integrated design of measurement systems has generally excluded consideration of strategies to optimize spatial and temporal coverage for different information requirements.

10.2.2.1 Increasing Demand for Greater Detail in Characterizing Pollution

Impact assessments necessarily deal with the behavior of pollutants over multiple spatial scales because important physicochemical processes occur on overlapping scales of space and time. Characterization of urban/neighborhood to regional scale pollutant gradients provides insight into the relative contributions of regional and local sources to local pollutant levels. However, matching actual pollutant exposure to individual groups of people or populations, a key link in the source to outcome accountability chain in Fig. 3.2, requires considerable detail on neighborhood-scale spatial and temporal variations, as well as indoor, outdoor, and human activity components. Likewise, most of the cases of ecological stress require information on atmospheric input to aquatic and terrestrial systems on a relatively small scale that matches certain geochemical vulnerabilities (e.g., Irving 1991, Chap. 6). Pollutants that are emitted directly from sources, which include CO, SO_2, NO_x, Pb, VOCs, a fraction of PM_x, and most of the HAPs, are subject to strong spatial and temporal gradients in the near-source region. These gradients can occur within areas of high population density, especially in urban areas. Characterizing the effects of these gradients on human exposure is of increasing concern for assessment of health effects (see also Chap. 5). Confidence in characterizing fine spatial and temporal scale concentration gradients may be an important factor in multipollutant risk assessments, as suggested in the EPA Detroit multipollutant air quality management study that is summarized in Chap. 13.

A better understanding of the role of long-range transport in local conditions has emerged in recent years. This includes an appreciation of the implications to air quality management of a gradual increase in continental and regional background pollutant levels. The potential significance of these contributions to North American air quality is magnified by the progress that has been made in air pollution abatement. Compounding the relative significance of transport and rising backgrounds condition is the adoption of increasingly stringent air quality standards in Canada and the United States. Consequently, observations that enable characterization of pollutant inflow and outflow across North American borders, as well as the global-scale observations of continental background levels, are increasingly relevant to North American air quality management.

10.2.2.2 Relevance of Spatial and Temporal Variations to Human Exposure

Two factors are central to characterizing the effects of ambient air pollution on human exposure: (1) people spend most of their time indoors, and (2) gradients of some pollutants in urban areas can lead to large variations in outdoor and indoor exposure. Neither of these factors is reflected in current community-scale air monitoring.

Addressing the first factor requires personal monitoring coupled with detailed knowledge of indoor pollutant emissions, outdoor air penetration rates, and time activity for population cohorts to understand and model exposure. Such work is generally beyond the scope of air quality monitoring programs, but it is often undertaken in specialized health-effect studies (e.g., Lower Fraser Valley, BC, Brauer and Brook 1997; Riverside, CA, PTEAM; Ozkaynak et al. 1996; Baltimore, MD, Bahadori 1998; Steubenville, OH, Connell et al. 2007; Birmingham, AL, Lachenmyer and Hidy 2000; Toronto, ONT, Kim et al. 2006a). These studies are expensive and labor intensive, and financial support has not been sufficient to study a range of human subjects, housing conditions, and construction practices while taking into account climatic differences, activity patterns, and seasonal influences. Nevertheless, such studies do inform the development of exposure models and the quantification of exposure errors, both of which can then be applied elsewhere given the appropriate input data. There is also some evidence that one can separate indoor exposure from outdoor exposure for some pollutants, such as $PM_{2.5}$, using sulfate as a tracer (Ebelt et al. 2005). Even with the studies of exposure noted above, there is little knowledge about how long-term exposure patterns are affected by changes in place of residence or socioeconomic conditions.

Addressing the second factor requires resolution of ambient exposure conditions via measurements with fine spatial resolution, traditionally referred to as neighborhood scale. However, limited resources prevent sustaining such measurements for a long period of time. Recently, investigations of intra-urban variations in exposure and effects have been undertaken using specialized field research programs and GIS-based exposure modeling methods. Examples of such work include studies conducted under the ARIES program in Atlanta (EPRI 2005), the Steubenville, Ohio SCAMP study (Connell et al. 2007), further analysis of the American Cancer Society Cohort (Jerrett et al. 2006), and a series of studies in the Toronto area (Brook et al. 2008; Jerrett et al. 2009) and Vancouver (Henderson et al. 2007; Brauer et al. 2008).

Despite their limitations, ambient monitoring networks have provided the primary data resource to support a broad range of epidemiological and risk assessment studies associating health responses to pollutant exposure. These studies have historically used air monitoring data from a single or a limited number of centrally located urban stations as a surrogate of human exposure (see Chap. 5). In using such measurements as a surrogate or proxy for human exposure, the assumption is made that for the exposure time window of interest the air a person or the population under study breathes is related quantitatively with outdoor air as indicated by the measurements at the central site. A key challenge in multipollutant epidemiological studies is that such relationships can differ considerably among pollutants, leading to differing errors in characterizing exposure. This issue, along with confounding factors due to correlation between variables, greatly hinders the ability to isolate the potential level of effect due to each pollutant in the mixture. Consequently, stronger health effect associations are often found for the pollutants with smaller exposure errors. $PM_{2.5}$ mass concentration presents a special challenge in that concentrations can be elevated indoors as well as outdoors, but one does not necessarily cause the other. In fact, studies have shown that similar PM concentrations in different urban areas can lead to significantly different PM-associated health effects.

Assigning a meaningful exposure to a person or a population based upon a limited number of outdoor monitors is complicated by differing individual daily activity patterns as people travel from their residences to work or other activities. Furthermore, over long periods of time, many people move their residences and workplaces to alternative geographical locations, making their chronic exposure increasingly uncertain without detailed residential and occupational history. Only health studies that track specific subjects to obtain information on their activities are able to deal with these issues. Cohort and panel studies are generally the methods that can achieve this level of exposure detail, but both designs have their own limitations and both require the use of specialized exposure measurements or exposure modeling to obtain more precise single or multipollutant exposures for each subject.

Continuing research is being conducted in the United States and Canada to improve exposure modeling and more effectively characterize population exposure using these models (see Chap. 5). In the meantime, the outdoor air measured either by a single ambient monitor, or a set of monitors in a given city, is considered the basis for risk assessment of pollution exposure; and it drives current regulatory goal-setting and measurement programs. The use of routine monitoring measurements for characterizing exposure in health-effects studies and the need to enhance these studies through more extensive air monitoring is likely to be debated, but unresolved, over the foreseeable future. However, adding a requirement to accurately characterize differential exposures to multiple pollutants through measurements alone is beyond the scope of any realistic air pollutant monitoring program. Thus, advancement in the model characterization for both single and multipollutant exposure that will be needed to address multipollutant air quality management at *Level 3* and *Level 4* (as discussed in Chap. 3) will require the application of improved exposure models supported by innovative approaches to air quality monitoring.

10.2.2.3 Vertical Resolution

Evidence accumulated through field campaigns has demonstrated the importance of pollutants throughout the atmospheric boundary layer and free troposphere to the persistence or changes in ground level concentrations. Therefore, routine characterization of pollution conditions aloft is an important adjunct to surface monitoring for short-term forecasting of pollution events and for longer-term prediction of the effects of air quality management actions. With the exception of routine meteorological soundings, vertical profiling of air pollutants and precursors through the atmospheric boundary layer and free troposphere is sparse and limited mainly to specialized field campaigns. Even when they are available, atmospheric column-depth and vertically resolved profiles of air quality and meteorological parameters typically lack temporal and spatial resolution. The twice-daily rawinsonde and ozonesonde measurements can miss key periods of boundary layer evolution and transients in wind important for evaluating air quality models. Polar orbiting satellites typically provide one and sometimes two instantaneous readings per day for a specific location. Limited temporal resolution makes it difficult to integrate space-based measurements with surface systems that typically provide time averaged or near continuous outputs at specific points.

10.2.2.4 Constraints on Temporal Resolution

Temporal resolution for a given measurement parameter can be limited by technical constraints or regulatory issues. The former limitation results from a range of issues beginning with the sensitivity of instrumentation or sampling methods through the difficulty in capturing the scales of meteorological and chemical processes in the atmosphere. The latter limitation results from the nature of the regulatory goals in terms of the required compliance metric and averaging requirements and the fact that the measurement method and sampling frequency may be specified by the regulatory authority. This mix of resource, technological, and sampling constraints may preclude implementation of a more ideal ground-based observation system that accommodates the range of time periods needed to elucidate important process features or effects.

Criteria pollutant gases of interest are generally measured continuously. Averages of these data can readily be achieved automatically in the data acquisition software. The strengths and weaknesses of such measurements are addressed, for example, by Parrish and Fehsenfeld (2000). Measurement of gaseous pollutant precursors, such as VOCs, is made using canisters and cartridges (with typical 3- to 24-h sampling periods) or by continuously operating gas chromatographs. There has also been an increase in the use gas denuders (24-h sampling periods) to establish baseline ambient ammonia concentrations and to account for volatile components of PM_x.

A recent example of the consequences of temporal constraints on pollution monitoring is exemplified by the case of monitoring particulate matter for different size classes (PM_x). The need for temporal resolution of observations is particularly strong for PM_x. Attention to PM_x conditions has increased with recent findings regarding its effects on human health (Peters et al. 2001)[1], as well as with our developing understanding of multiscale atmospheric processes. North American networks have deployed over 500 routinely operating continuous $PM_{2.5}$ mass samplers. However, the use of these sites to characterize the distribution of particle concentrations across broad spatial regimes is complicated by the deployment of different instrument technologies and operating parameters. The instruments themselves can impart potentially false spatial and seasonal differences due to variable volatility losses. Harmonization with reference methods (the filter-based, gravimetric technique) may catalyze greater use of continuous data. Both methods have their limitations and inherent uncertainties; nevertheless, the science is advanced to the point where these differences are well documented and understood.

Routine PM_x bulk chemical speciation networks in the United States acquire 24-h average filter-based samples, every third or sixth day. This design is adequate for monitoring relevant to an annual $PM_{2.5}$ standard and the U.S. regional haze program, but it can limit the level of precision applied to the 24-h standard. Intermittent sampling can also limit evaluation of acute health effects, emission variability, development of air quality models, application of some source attribution techniques (see also Chap. 9), the study of atmospheric processes, as well as the study of human health response.

Several special studies emerged in the late 1990s; these studies began systematically evaluating continuous measurements of PM_x chemical properties and repre-

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[1] Health scientists have pressed for shorter time resolution of ambient data, but their analyses are limited by recording of health markers, such as mortality and morbidity. These appear to be on the scale of days and longer. Thus hourly averaging appears to be primarily a concern for characterizing dynamics of atmospheric processes, and perhaps acute response to short term exposures.

sented a transition from the emphasis on the oxidant studies conducted during the prior two decades. The $PM_{2.5}$ Supersites program (Pandis et al. 2005; Solomon et al. 2008) spurred the testing and development of a variety of continuous aerosol mass, chemistry, and physical-property measurement technologies. However, there has not been a sustained effort to deploy and maintain semi-continuous particle speciation instruments, with the notable exception of the SEARCH/ARIES (EPRI 2005; Hansen et al. 2003).

In addition to mass and bulk chemical composition, physical properties other than mass are important measurement parameters. For example, there is increased interest in the effects of exposures to ultrafine particles (<0.1 μm diameter). Exposure concerns relate not only to the chemical species present in this size range, but also to the possible influence of the number of and type of inhaled particles. In addition to health concerns, ultrafine particle observations are relevant to particle formation processes, including new particle formation (nucleation) and growth. These concerns suggest that monitoring total particle number and size distribution is important. Furthermore, evidence indicates that particle number and size are sensitive to source emissions or inputs such as vehicle fuel changes and engine control technologies (e.g., Wahlin et al. 2001). This evidence implies that such measurements are highly relevant for tracing emission changes due to such technology shifts and for studying their exposure and effects. These data would also aid in retrospective studies of regulatory effectiveness and accountability.

Recent advances in instruments that produce cost-effective and reliable estimates of particle number and surface area (McMurry 2000; McMurry et al. 2004) offer potential for routine network operations. However, advanced continuous speciation and particle property measurement technologies largely remain research tools. Barriers to implementing continuous speciation technologies include (1) a focus on mass-based compliance standards, which diminish the perceived regulatory value of continuous measurements, (2) technology issues related to measurement quality and reliability, and (3) cost effectiveness. Market incentives and resource support for continuous sampling technologies are limited, and would benefit from increased government support.

10.2.3 Accounting for Hazardous Air Pollutants

Combining measurements of criteria and hazardous air pollutants presents many measurement challenges. These include the number of instruments required, the wide range of detection limits, the differing spatial and temporal scales over which different pollutants may affect vulnerable receptors, and the need to establish some priorities among the list of hazardous pollutants (the list of U.S. HAPs, for example, can be found in the List of Terms).[2] From a multiple pollutant perspective, there may

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[2] Air toxics listed for Canada and Mexico differ from those adopted in the United States as HAPs. They also are defined in the List of Terms.

be a need to determine concentration patterns of HAPs on the same scale as criteria pollutants, as the former are not well represented in most networks. As summarized later in Chap. 12, the United States and Canada have measured a subset of HAPs on an intermittent basis as part of the PAMS and NAPS monitoring programs. These measurements have also included some of the metals found in particles. Mexico, on the other hand, has just begun to focus attention on air toxics, mainly in Mexico City. Routine monitoring of persistent, bio-accumulating, toxic substances (PBTs) is limited to a few sites (e.g., Integrated Atmospheric Deposition Network—IADN) around the Great Lakes. The Mexican Dioxin Air Monitoring Network (MDAMN), a joint effort of Environment Canada, EPA, and INE/SEMARNAT, was established in March 2008 to measure dioxin, furan and coplanar PCB concentrations in air (Wöhrnschimmel et al. 2008). HAPs measurement in the United States, with the addition of over 25 National Air Toxics Trends sites (NATTS), provides an example of a sustained commitment for multipollutant observations, including specific air toxins.

Extensive monitoring of all HAPs is probably not necessary and not economically practical in a resource-limited environment. Consequently, some sort of priority setting, probably based on risk, would be required in order to include HAPs in a multipollutant management program. From the measurement perspective, information on the practicality of including HAPs in a comprehensive multipollutant approach can be gleaned from past experience. For example, some state and provincial laboratories perform HAPs analyses, with a variety of measurement protocols and consequent data comparability problems. Comparability is complicated by typically very low concentration values, approaching or falling below measurement quantification limits. The wide range of contaminant concentrations found in the atmosphere poses a formidable challenge to the measurement community for designing and maintaining routine air monitoring capability addressing regulatory requirements. Table 10.1 lists typical measurement ranges for CPs and HAPs, along with measurement methods and the lower limits of quantification that potentially are possible for the respective species. This tabulation implies that within today's instrumentation technology the typically higher ambient concentrations of the CPs are more readily measurable and have less uncertainty than their much more dilute HAPs counterparts. Thus, strategies for monitoring most CPs can employ continuous methods with confidence while most of the HAPs require sampling by some form of pre-concentration or sample-averaging over a period of at least 24 h or longer.

HAPs are generally identified with specific or common sources. Many of these species derive from specific or certain chemical process technologies, but others have a more common origin such as in motor vehicle exhaust or commercial-industrial operations more or less universally present in urban areas (e.g., Chap. 8). The motor vehicle class forms a grouping that is often added to ambient concentrations measurements across national systems. For example, among the air toxics commonly found in motor vehicle exhaust, observations of benzene and other aromatics are widespread and reported in VOC monitoring. However, other potentially important species are less well represented. During the initial startup of the NATTS, six priority HAPs (formaldehyde, benzene, 1, 3-butadiene, hexavalent chromium, acrolein, and arsenic) were targeted for inclusion, based on results of the 1996 National Air

Table 10.1 Illustrative list of typical urban concentrations of criteria pollutants compared with some air toxics, along with their typical quantification limits

Pollutant	Typical range of concentrations (hourly values, unless noted)	Measurement technique	Typical lower limits of quantification
Ozone	10–200 ppb	UV Photometry	3 ppb
Sulfur dioxide	0.5–100 ppb	UV fluorescence	0.5 ppb
Nitrogen oxides	0.5–200 ppb	Chemiluminescence	0.5 ppb
Carbon monoxide	100–1000 ppb	Non-dispersive infrared spectrophotometry (NDIR)	50 ppb
Fine particles	5–200 µg/m^3 (24 h)	Gravimetric	2 µg/m^3
Lead	0.01–1 µg/m^3(24 h)	TSP/glass fiber with AA[a] or ICPMS	0.43 ng/m^3 (lo) 0.02 ng/m^3 (hi)
HAPS			
Formaldehyde	2.0–3.8 µg/m^3 (24 h)	Dinitrophenylhydrazine (DNPH) coated sorbent tubes with HPLC analysis	0.01 µg/m^3
1,3-Butadiene	95–240 ng/m^3 (24 h)	Canister; analysis by Gas Chromatography/Mass Spectrometry (GC/MS)	0.08 µg/m^3
Benzene	0.74–1.5 µg/m^3 (24 h)	Canister; analysis by Gas Chromatography/Mass Spectrometry (GC/MS)	0.11 µg/m^3
Benzo(a)pyrene (PM10, stp)	0.062–0.15 ng/m^3 (24 h)	Filter/PUF/XAD2; analysis by Gas Chromatography/Mass Spectrometry (GC/MS)	0.12 pg/m^3
Trichlorethylene	0.13–0.23 µg/m^3 (24 h)	Canister; analysis by Gas Chromatography/Mass Spectrometry (GC/MS)	0.14 µ/m^{3}g
Vinyl chloride	0.060–0.13 µg/m^3 (24 h)	Canister; analysis by Gas Chromatography/Mass Spectrometry (GC/MS)	0.09 µg/m^3
Carbon disulfide	0.16–1.3 µg/m^3 (24 h)	Canister; analysis by Gas Chromatography/Mass Spectrometry (GC/MS)	0.04 µg
Arsenic (PM10, stp)	0.86–10 ng/m^3 (24 h)	47 mm Teflon filter or 8 × 10″ quartz (lo and hi vol, respectively)/Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)	0.28 ng/m^3 (lo) 0.01 ng/m^3 (hi)
(Hexavalent) Chromium	0.01–0.88 ng/m^3 (24 h)	Acid washed bicarbonate coated cellulose filter; analyzed by Ion Chromatography (IC)	0.008 ng/m^3
Nickel (PM10, stp)	1.7–4.1 ng/m^3 (24 h)	47 mm Teflon filter or 8 × 10″ quartz (lo and hi vol flow, respectively)/ Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)	0.88 ng/m^3 (lo) 0.09 ng/m^3 (hi)
Mercury (PM fractions)		Filter collection followed by ICP/MS (PM10 and TSP) or XRF[a] (PM$_{2.5}$ speciation sites)	Unreliable data through filter based sampling
Mercury total dry Hg^0 (g), Hg^{+2}(g),pHg	Hg^o 1.4–1.6 ng/m^3 Hg^2 10 pg/µm^3	Semi-continuous through TEKRAN; gold adsorbent followed by thermal desorption and detection through Cold Vapor Atomic Fluorescence Spectrometry (CVAFS)	Hg^2 approaches Hg^o levels in free troposphere and near sources

[a] *AA* atomic absorption spectroscopy; *XRF* x-ray fluorescence spectroscopy

Toxics Assessment (NATA; http://www.epa.gov/ttn/atw/nata/). Furthermore, based on interests in community exposure issues, efficiencies in methodologies and the 1999 NATA, NATTS observations were expanded in the United States to include:

> Acrolein, perchloroethylene, benzene, carbon tetrachloride, chloroform, trichloroethylene, 1, 3-butadiene, 1, 2-dichloropropane, dichloromethane, tetrachloroethylene, vinyl chloride, formaldehyde, acetaldehyde. nickel compounds (PM_{10}), arsenic compounds (PM_{10}), cadmium compounds (PM_{10}), manganese compounds (PM_{10}), beryllium (PM_{10}), lead (PM_{10}), hexavalent chromium (TSP), and benzo(a)pyrene.

As noted in the NATA, reliable routine methods are not available or remain unproven for some of the higher priority HAPs (e.g., acrolein and hexavalent chromium). Sampling issues associated with capture efficiency and sample deterioration remain for acetaldehyde, formaldehyde and 1, 3-butadiene. Carbonyl measurements (acetaldehyde and formaldehyde) from the PAMS program have provided additional spatial coverage relative to other HAPs, though the sampling techniques are relatively labor intensive and are subject to uncertain interference and collection efficiency errors.

In partnership with state and local agencies, EPA commissioned a study from 2000–2001 (Battelle 2001) to review the quality of HAP measurements performed by monitoring programs in the United States. One of the conclusions from this study was that the majority of HAPs data is not suitable for most interpretive applications, given the inconsistency across laboratory protocols, lack of confidence in sampling or analytical methods, and many reported observations below quantification limits.

In addition to the complexities in measurement methods, air toxics provide significant challenges associated with the variety of species often associated with different localized spatial scales or unique source features (see also Chap. 8). Groupings of HAPs exist, based on source origin and chemical properties (Chaps. 7 and 8), and these suggest an approach for incorporating them in a multipollutant air quality assessment. Several of the ozone precursor compounds measured in PAMS are HAPs species as well, and in many cases they share common emission sources. These commonalities suggest the need for developing comprehensive, integrated, and value-added measurement programs that complement existing monitoring networks. Ideally, basing a measurement program on these commonalities could increase the specificity of pollutant composition in time and space and serve as a basis for the design of an optimized, integrated multipollutant measurement system.

10.3 Measurement Needs for Multipollutant Air Quality Management

Several measurement improvements are needed to support multipollutant air quality management at *Levels 1* and *2* and beyond. These include an increased emphasis on speciated VOC measurements, measurements of speciated oxidants, organic aerosols, black carbon and nitrogen oxide species. The importance of such observations in a multipollutant air quality management environment is discussed in the following sections.

10.3.1 VOC Measurements in Representative Areas

The PAMS network remains the primary source of routine speciated urban VOC data in the United States. In the United States, the PAMS and air toxics networks provide data on selected VOC HAPs in many major (e.g., population > 500,000) urban cities. A substantial, but intermittent, record of VOC measurements from the research community has also been compiled through field measurement campaigns over the past decade, utilizing sampling canisters or other in situ instrumentation. These campaigns have ranged from city-specific, to regional, to global in scale (e.g., Parrish et al. 1998; EPRI 2005; Warneke et al. 2007), although the motivation for the measurements has been driven principally by the desire to improve knowledge of atmospheric photochemical oxidation processes rather than to understand their implications for assessing air quality management decisions.[3] Through the NAPS, there also are geographic and annual coverage for VOCs in Canadian cities and a few rural areas in Canada. In Mexico, intermittent measurements of speciated VOCs have been made during special studies within Mexico City and along the U.S.-Mexico border.

Existing VOC observations provide a baseline level of knowledge for air quality management and accountability analyses of ozone management actions, and they provide some basic information for understanding emissions of volatile and non-volatile organic species. Speciated VOC measurements are mostly limited to metropolitan areas in North America, and analysis of these data have shown that hydrocarbon composition profiles are relatively uniform across urban areas, reflecting the ubiquitous nature and significant influence of mobile source emissions (Parrish et al. 1998). Analysis of hydrocarbon speciation profiles outside of urban regions, areas, on the other hand, consistently shows local depletion in the more reactive anthropogenic compounds (e.g., olefins and aromatics). The relative ratios of select compounds with distinctly different reactivity (e.g., with respect to OH) measured at non-urban sites has proven informative in characterizing the (chemical) age of the air masses sampled (Goldstein et al. 1995; Gong et al. 1997; Parrish et al. 1998). While the photochemical questions are important to oxidant management, the HAPs contained in the measured VOCs are also important for multipollutant characterization.

Addressing accountability of measures for controlling VOC emissions and the effectiveness of these controls in reducing ozone concentrations remains problematic for the following reasons: (a) PAMS measurements came on-line (ca. 1995) after many of the major VOC controls had been implemented (e.g., exhaust catalytic convertor, evaporative emission controls and reductions in Reid vapor pressure of

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[3] The ARIES VOC data are long term and have been collected between 1999 and 2008 in Atlanta, GA for basic speciation, and for integrating into epidemiological studies of air quality in the city.

gasoline); (b) post-1990 VOC emissions (using reformulated gasoline) for light-duty vehicles are quite small, adding difficulty for quantification in ambient air; and (c) the precision and accuracy of PAMS hydrocarbon measurements (Parrish and Fehsenfeld 2000; Fortin et al. 2005) may not be sufficient to track the emission changes relative to a "noisy" background affected by intra- and inter-annual variations in meteorology and varying traffic patterns.

Anthropogenic hydrocarbon emissions, however, are not the only reactive VOCs affecting ozone production, especially on the regional scale. Over the last two decades, investigators have recognized the importance of biogenically emitted VOCs (e.g., isoprene, terpenes, sesquiterpenes) in photochemical processes, and their contribution to $PM_{2.5}$ mass via secondary organic aerosol formation (e.g., McMurry et al. 2004; Seinfeld and Pandis 2006). The PAMS network reports isoprene concentrations but not other biogenic compounds. The Canadian NAPS, on the other hand, reports both isoprene and terpene concentrations. Although affected by anthropogenic emissions, particularly mobile source emissions, rural measurements of VOCs show a large and variable fraction of biogenic species (e.g., isoprene and terpenes) relative to total VOC concentrations. However, measurement methods for terpenes and sesquiterpenes having high reactivity remain problematic and monitoring of these species is not performed on a routine basis. Better characterization of biogenic VOC species in rural and regional environments is needed to assess their contribution to the formation of regional ozone, secondary organic aerosols, and associated photochemical processes and oxidation products.

Current measurements of formaldehyde following the PAMS protocol are subject to substantial sampling artifacts that compromise our ability to characterize many of the process and exposure issues associated with this pollutant. The sources of ambient formaldehyde include motor vehicle emissions and the photochemical oxidation of anthropogenic and biogenic hydrocarbons found in the atmosphere. Formaldehyde is emitted in the exhaust of both gasoline and diesel powered engines, but these emissions are enhanced in the tailpipe emissions of ethanol containing fuels. In addition to being a hazardous air pollutant, formaldehyde is a useful diagnostic species for assessing the reliability of emission estimates as well as the chemistry in air quality models. Estimates of formaldehyde formation from oxidation of isoprene in conjunction with satellite-based estimates of formaldehyde concentrations have been used to estimate large-scale biogenic isoprene emissions across the United States (Palmer et al. 2003).

10.3.2 Speciated Oxidants

A potentially important but unanswered question for multipollutant exposure is the significance of exposure to highly reactive, photochemically generated oxidants other than ozone. These oxidants include hydrogen peroxide (H_2O_2), other peroxides, and transient free radical species from OH to RO and RO_2, R being an alkyl chain. These species are rarely measured, except in specialized field campaigns.

However, they are well known to be present in the lower troposphere as part of the photochemical cycle. They are associated with at least one hypothetical health factor, involving the presence of peroxides as transient oxidizers in humans. H_2O_2 in particular is a measure of a photochemical chain reaction termination pathway, and it is involved in the aqueous atmospheric oxidation of SO_2 to form sulfate. Better data on the ambient concentrations of these oxidants could be used not only for health relevant studies, but also for investigating the details of chemical mechanisms in air quality models. To facilitate systematic investigation of these species as health and ecosystem stressors, design of an enhanced oxidant monitoring program should be considered as a supplement to existing ozone measurements in North America.

10.3.3 Organic Aerosol Composition

Atmospheric particles can contain hundreds to perhaps thousands of organic compounds, including a variety of oxygen, sulfur, nitrogen, and adsorbed VOC species. It is likely that organic components have changed over time, and will change in the future as fuel mixtures, industrial emissions, and emission controls continue to evolve. Current speciation networks typically measure aggregated total organic carbon levels, because it usually is not practical to measure large numbers of organic components in the condensed phase. In fact, only about 25–30% of the organic carbon fraction has probably been identified (Seinfeld and Pandis 2006). Nevertheless, key molecular markers of the organic carbon fraction of PM do exist, and they have been used in a variety of source-apportionment applications (e.g., Schauer and Cass 2000; Brook et al. 2007). Sampling and analysis for organic particle composition at a modest grouping of sites, with limited sampling frequencies and current research instrumentation, could supplement current routine analyses for bulk chemistry, and improve the multipollutant characterization of PM material, both for human exposure and for source identification.

10.3.4 Reactive Nitrogen Species

Characterization of atmospheric nitrogen compounds is important to environmental assessments of ozone, aerosols, acidification, eutrophication, and visibility impairment. In addition, organo-nitrogen compounds are probably important health stressors, although their importance is not well delineated. There are numerous shortcomings in our NO_x observation systems—a chronic concern considering that NO_x emission reductions have been a major factor in North American air program rules over the last decade. In the United States, for example, a reliable long-term observation base does not exist to determine whether ambient NO_x response (especially as NO_2) is consistent with measured or projected emission changes. Although NO_x emissions from power plants are well known in the United States because they are measured by continuous emission monitoring systems, the ability of existing ambient urban NO_x measurement networks to detect NO_x emission changes associated with power plant emission reductions is compromised by strong local mobile-source NO_x emission signals.

Total reactive nitrogen (i.e., NO_y, is the sum of all oxidized nitrogen species—NO, NO_2, peroxyacetylnitrate [PAN], HNO_3 and other trace species such as HONO, and N_2O_5)[4] represents most if not all of the gaseous nitrogen budget, and it is a useful ambient indicator for tracking the fate of emitted NO_x and supporting a variety of observational and emission-driven air quality models. Although NO_y has been measured for over twenty years in field campaigns, with but a few exceptions (e.g., the SEARCH network and selected CAPMoN sites) routine long-term NO_y observations have not been performed in North American networks. True NO_2 is an important diagnostic species for atmospheric chemical processes (Fig. 7.1). Although NO_2 is a criteria pollutant, it is not accurately measured. NO_2 data from most U.S. regulatory monitoring sites are compromised by interferences from other oxidized nitrogen species. “True” NO_2 is measured directly at some Canadian locations and by the SEARCH network. Furthermore, resolution of reactive N species including PAN and nitric or nitrous acid (HNO_3, HONO) would provide valuable insight into atmospheric processes. Nitric acid is an important oxidant species in the atmosphere, and is an indicator of one chain reaction termination pathway in photochemistry. Better knowledge of ambient HNO_3 and HONO concentrations would also improve our ability to investigate the human health consequences of oxidant exposure to these compounds, diagnose a number of processes related to ozone production and deposition in urban environments, and help resolve and account for the nitrogen budget and regional transport corridors.

The range of reactive N composition in rural air is shown for two Canadian sites in Fig. 10.2. These measurements began before 2003 and continue to be collected at these sites plus a third location. Short-term studies also have been undertaken at a limited number of locations to assess differences between NO_2 as determined from typical NO_x monitoring instruments and true NO_2, and to assess the relative role of NO_z (NO_y–NO) species. The complexity of nitrogen oxide speciation clearly indicates that added detail about reactive nitrogen species would be an important addition to air monitoring, even if obtained at a small number of urban and rural sites across North America for a range of photochemical environments.

Nitrate radical ($NO_3\cdot$) is believed to be an important nighttime oxidant affecting long-range transport of ozone and ozone precursors. Measurements of $NO_3\cdot$ at one or two representative locations would enable diagnosis of model reliability relative to overall nitrogen balances and secondary aerosol particle formation. Reliable ground-based $NO_3\cdot$ measurements using DOAS have been demonstrated over the past 20 years, including year-round sampling in Berlin (Geyer et al. 2001), at a

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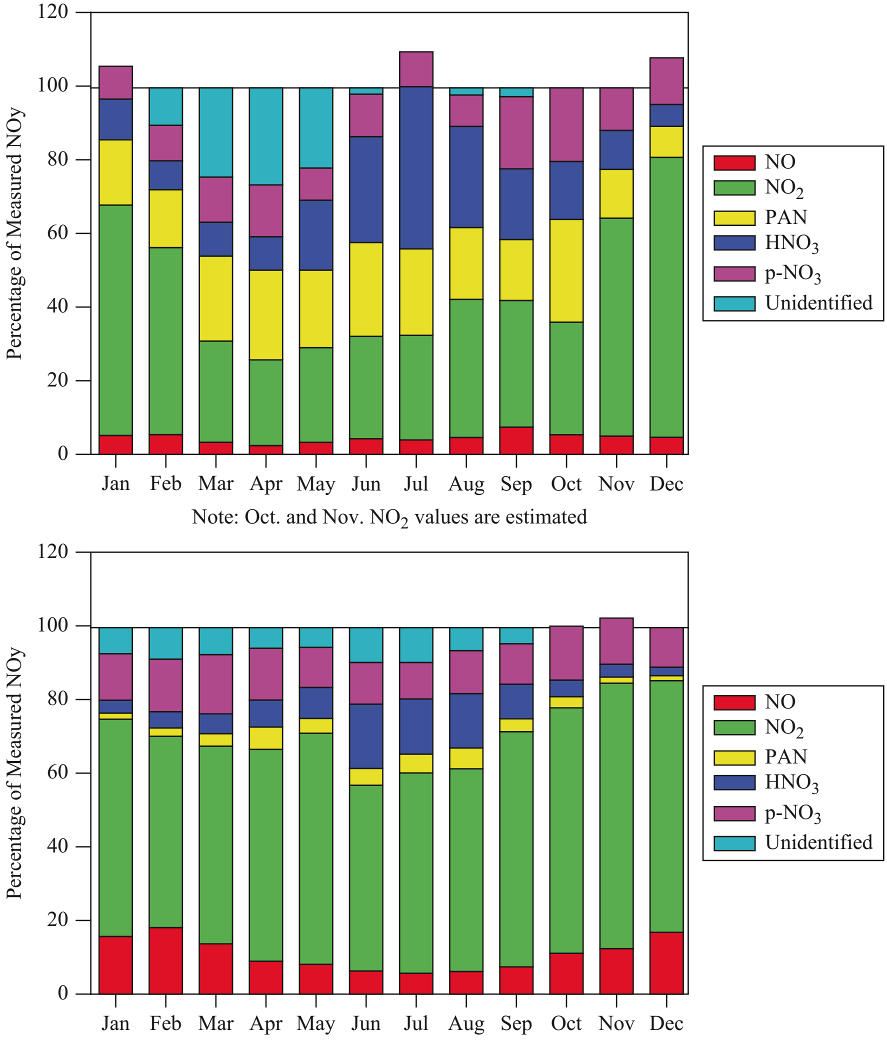
[4] Since the late 1990s, reliable measurements of NO_y have been reported for a number of sites in recent NOAA campaigns (e.g., Parrish and Fehsenfeld 2000), and in the Southern Oxidant Study (SOS) research. Since the late 1990s, long-term measurement of NO_y has taken place in the southeastern SEARCH network (e.g., Hansen et al. 2003).



Note: Oct. and Nov. NO_2 values are estimated

Note: Jan. and Feb. PAN values are estimated

Fig. 10.2 Examples of the relative abundance of several NO_y species measured at two rural southeastern Canadian sites as a fraction of the total measured NO_y concentration—Kejimkujik, NS, (*top*) and Egbert, ON, (*bottom*) during 2003. (Source: Environment Canada 2009)

remote site on the Baltic Sea (Heintz et al. 1996), and in the Lower Fraser Valley of British Columbia (McLaren et al. 2004). However, these methods have not been incorporated into routine monitoring practice.

Nitrous acid is known to be an important generator of OH radicals (e.g., Demerjian et al. 1974; Stutz et al. 2004; Ren et al. 2003) with potential for health stress (Beckett et al. 2005). Ambient measurements of HONO over the past decade suggest important production pathways from heterogeneous atmospheric reactions as well as direct emissions (e.g., Li et al. 2008; Harrison et al. 1996), neither of which are characterized satisfactorily by mechanistic analysis and existing air quality models.

In addition to NO_y, the reduced nitrogen species, such as ammonia and particulate ammonium, are important components of the overall nitrogen species mass balance relevant to PM exposure. Reduced N is particularly important to fine-particle formation, visibility and ecosystem impacts. Ammonia emission estimates remain highly uncertain and reliable ambient ammonia measurements are sparse. Most ammonia measurements have been associated with emission-flux estimations from agricultural sources. Currently, particulate ammonium is analyzed as part of some chemical speciation programs, but ammonia volatilization within the filter sampler and during filter handling creates a potential bias in the reported data. This bias has been investigated in the U.S. Supersite program as well as in SEARCH and NAPS by employing ammonia denuders in samplers. At selected CAPMoN sites, additional citric acid filters are being included in the filter packs to measure 24-h averaged NH_3 concentration. Recently, considerable knowledge of ambient NH_3 concentrations and emissions was obtained from a three-year initiative by Agriculture Canada and Environment Canada. Finally, continuous NH_3 monitoring procedures have improved, enabling continuous NH_3 observations at some sites, for example, in New York (e.g., Schwab et al. 2008).

10.3.5 Carbon Monoxide and Sulfur Dioxide

The measurement needs described in the previous sections primarily support source identification and reaction chemistry for oxidants and $PM_{2.5}$ component formation. Two criteria pollutants that are often "forgotten" in the design of new measurement programs are CO and SO_2[5]. Ambient concentrations of these two pollutants are usually considered to be sufficiently low in urban areas that they are of minimal interest to urban air quality management practice. However, both are important as local and regional indicators of source contributions to ambient air. Thus providing measurement of these pollutants at concentrations well below those of concern for regulatory compliance is important for supporting analyses of source receptor relationships. Measurements of CO and SO_2 are essential for establishing trends in these criteria pollutants in relation to changes in source emissions. In North America the primary source of SO_2 and CO is the combustion of fuels, which also produce emissions important to photochemical oxidant and particle formation cycles (cf. Chap. 7). Consequently, these gases are important surrogates for other

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[5] A 2010 proposed U.S. SO_2 standard targets a 1-h daily maximum between 50–100 ppbv based on a three-year average of the 99th percentile (4th highest concentration), vacating the existing 24-h and annual NAAQS.

pollutants and are often used in characterizing single pollutant exposure. If mobile source fuels are sufficiently low in sulfur, these gases can also provide tracers for differentiating between local and regional mobile (CO) and stationary source (SO_2) signals. They also are important slow reacting species for model evaluation. CO often is used as a surrogate for other co-emitted low reactivity toxic species which are difficult to measure. SO_2, in combination with particulate sulfate, is the major component of sulfur budgets used in characterizing airborne sulfur oxide (SO_x) exposure and ecosystem deposition assessments. Analysis of SO_2 concentrations can provide an indicator for aging of air masses influenced by coal-fired power plant emissions using the sulfate to SO_2 ratio. Measurements of SO_2 also provide information for evaluating model-estimated sulfate production by comparing SO_2 precursor concentrations with underlying $PM_{2.5}$ sulfate mass fraction and visibility estimates. Ambient SO_2 concentrations also are used in parameterization schemes characterizing ammonia deposition in air quality models. Reliable tracking of SO_2 trends also has important accountability implications given continued efforts to reduce sulfur in fuels (off-road diesel, ocean-going ships) and SO_2 emissions from power generation.

Current measurements of SO_2 and CO are largely sited in urban areas and often made in proximity to major source areas, which limits their usefulness in characterizing broader scale spatial domains. As mentioned previously, SO_2 and CO monitoring has been designed to provide measurements in areas estimated to have relatively high concentration levels in order to document compliance with health-based ambient air quality standards. In general, the instruments used are not sufficiently sensitive to provide quantitative measurements in well-mixed urban and rural environments where concentrations of these pollutants are generally very low. Consequently, many existing networks lack representative and reliable measurement of these valuable indicator species. Their use in evaluating the reliability of air quality models and emission inventories and for computing sulfur and carbon balances is important as well. Theoretically, measurements of CO and SO_2 could also provide a surface-based concentration "calibration" for interpreting total atmospheric column observations from remote sensing observations, including those from satellites.

10.4 Advances in Instrumentation Facilitating Multipollutant Management

The current monitoring approaches used by networks in the United States follow legally sanctioned standard or federal reference methods, some of which were developed decades ago. These approaches are often adopted by Canadian and Mexican monitoring networks as well, although there is usually not a legal requirement to deploy a specific method. Reference and equivalent methods often require skilled field technicians and extensive laboratory capabilities for analyzing samples acquired in the field. A hierarchy of quality control and assurance procedures is applied to ensure that the measurements are quantitatively reliable, comparable across networks, and traceable to reference standards.

The deployment of new advanced instrumentation into monitoring networks has the potential for improving the operational efficiency and effectiveness of the systems for multipollutant characterization. As exemplified in Table 10.2, a number of instruments have been demonstrated for use in the field and are either commercially available or potentially commercially viable for current applications at *Levels 1* and *2* and beyond. The development of new instrumentation has been motivated by the need for a better understanding of photochemical processes (e.g., NARSTO 2000), and by the promulgation of the 1997 U.S. $PM_{2.5}$ standards. Developments stemming from this research are now providing opportunities to improve the spatial and temporal coverage of multipollutant observations in North America and at the same time reduce the labor costs associated with such measurements (e.g., McMurry et al. 2004).

With any proposal to expand measurements to include groups of CPs and HAPs, it is important to examine current monitoring operations for opportunities to deploy new instrumentation. There are a number of instruments that have been field tested for research purposes since the 1990s and some have been deployed in air monitoring in programs such as SEARCH, the EPA Supersites program (Hansen et al. 2003; Solomon et al. 2008), and at selected CAPMoN sites. Most new methods are capital intensive, but in principle many could offer opportunities for reliable, simple operation that is less labor intensive in the field and may also reduce or eliminate work in the laboratory for sample-processing and chemical analysis.

A detailed description of all potential new methods is beyond the scope of this report. However, the examples in Table 10.2 illustrate that a variety of techniques could be considered in addressing a number of multipollutant measurement needs. If deployed properly, these newer technologies would add important observations. These observations would help fill some of the critical gaps across a variety of indicator categories, spatial scales, environmental media, and pollutant classes; and they would likely serve as an important step in a progression toward a more accountable multipollutant air quality management system. Thus, to achieve this goal it will be necessary to initiate new mechanisms for network design so that institutional barriers that constrain the addition of new measurement methods to existing operations do not hinder progress.

10.5 Integration Among Networks and Disciplines

Measurement programs developed as part of future multipollutant, results-based air quality management will need to take full advantage of the existing set of monitoring networks that are operated by numerous agencies. Viewing these networks as an integrated system will assist in identifying and filling important measurement gaps that limit our ability to achieve better spatial and temporal coverage and meet

Table 10.2 Examples of contemporary instrumentation for deployment in ground-based monitoring programs across North America

Species	Instrument principle	Reference
NO_2	Photofragmentation-chemiluminescence (PF-CL); Cavity Attenuated Phase Shift Spectroscopy (CAPS); Laser Induced Fluorescence (LIF); Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS); GC-Luminol	Parrish et al. (1990); Fehsenfeld et al. (1990); Kebabian et al. (2005); Cleary et al. (2002); Gaffney et al. (1998); Li et al. (2004); Thornton et al. (2000, 2003)
NO_y	Catalytic reduction-chemiluminescence	Fahey et al. (1985)
Formaldehyde (H_2CO)	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS); Diffusion scrubber/liquid fluorescence; Differential Optical Absorption Spectroscopy (DOAS)	Gilpin et al. (1997); Li et al. (2004); Herndon et al. (2007); Fan and Dasgupta (1994); Hak et al. (2005)
Formic acid (HCOOH)	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS);	Herndon et al. (2007)
NH_3	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS); Laser Photoacoustic Spectroscopy; Ion Mobility Spectroscopy; Wet Effluent Diffusion Denuder; Long Path Absorption Photometry (LOPAP)	Schwab et al. (2008); Fehsenfeld et al. (2002); Li et al. (2006); Hill et al. (1990); Genfa et al. (2000); Bae et al. (2007)
HONO	Photofragmentation-LIF; Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS); Long Path Absorption Photometer (LOPAP); Differential Optical Absorption Spectroscopy (DOAS)	Liao et al. (2006); Li et al. (2008); Zhou et al. (1999); Heland et al. (2001)
HNO_3	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) Chemical ionization mass spectrometer (CIMS) TD-LIF Scrubber difference-NO chemiluminescence	Horii et al. (2004); Neuman et al. (2000, 2002); Day et al. (2002); Yamamoto et al. (2001)
PAN	Gas Chromatograph-Chemical Ionization Detector Chemical ionization mass spectrometer (CIMS)	Gaffney et al. (1998); Williams et al. (2000); Slusher et al. (2004)
N_2O	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS);	Kroon et al. (2007); Waechter et al. (2008)

Table 10.2 (continued)

Species	Instrument principle	Reference
CH_4	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS);	Kroon et al. (2007)
$^{12}CO_2$, $^{13}CO_2$	Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS);	Nelson et al. (2008); McManus et al. (2005)
PM SO_4	Continuous Thermal reduction and Pulsed Fluorescence	Solomon and Sioutas (2008)
PM size and chemical composition	Aerosol Mass Spectrometer; High Resolution Time-of-Flight AMS	Jayne et al. (2000); Canagaratna et al. (2007); Gard et al. (1997)
PM OC	Thermal-optical	Bae et al. (2004);
	Thermal desorption GC-MS	Williams et al. (2006)
PM BC	Photoacoustic Spectrometer	Arnott et al. (1999)
	Single-particle soot photometer	Schwarz et al. (2006)
PM number and size distribution	Condensation particle counters; Differential mobility analyzers;	McMurry (2000)

An important additional category of measurement are the fast reacting intermediate oxidant species such as H_2O_2, organic peroxides and the free radicals, OH, RO and RO_2. These species are difficult to measure outside of a highly specialized research program. However, they are sufficiently important for future applications and accountability, that increased efforts are needed to obtain commercially viable instruments for these species the needs of the human exposure, health, and ecosystem assessment communities. Opportunities for such integration include:

- Improving exposure estimates by linking ambient observation measurement fields with human activity patterns to estimate exposures.
- Linking similar pollutants for spatial coverage by blending urban and rural-based networks including the networks across the three countries.
- Assimilating pollutants vertically through the atmosphere by blending of ground measurements, vertically resolved systems, and remote sensing to yield a combination of vertically resolved gradients through the boundary layer and into the free troposphere, and by improving surface-level resolution through correlation relationships between surface and column observations.
- Combining ambient air observations with wet/dry-deposition observation networks to develop total deposition fields, as performed currently through the CASTNET and NADP programs and CAPMoN.
- Aligning atmospheric deposition observations with soil and surface water measurements, particularly in areas of vulnerable ecosystems (see also Chap. 6).
- Co-locating different species measurements to yield multiple pollutant characterizations within a consistent spatial coverage.
- Creating a subset of sites using source-relevant instrumentation to document strong gradients in pollutants, which are of concern to health scientists and model developers.

Integration of measurement programs has progressed through ad hoc international working groups since the 1980s. Examples of integration among U.S. networks to improve spatial coverage include NAMS, CASTNET, and SLAMs; and the IMPROVE/STN rural and urban network pairs for surface ozone concentrations and aerosol speciation, respectively. These efforts have been particularly fruitful for investigating transboundary pollution transport in certain areas. Adoption of relatively minor adjustments in quality assurance protocols could improve integrated analysis of the ozone and PM_x speciation networks. However, much greater effort will be needed to provide reliable long-term data for NO_x and VOCs at key sites across North America. Thus, a fully integrated system, with attention to design and implementation for multipollutant air monitoring, remains in the future.

10.6 Demonstrating Accountability

Accountability assessments rely on self-consistent, long-term (perhaps over at least a decade or more) observations to capture a system's response to emission changes or other factors (see also the discussion in Chap. 12). Ideally, accountability should follow the sequence in Fig. 3.2, tracing emissions through ambient air quality to health or ecological effects. A number of observational gaps relevant to accountability assessments have been identified above. In this section the more systematic discussions on accountability in Chap. 12 are augmented, by considering the lessons learned from ozone mitigation policies from the standpoint of the availability of the appropriate measurements. The use of observations in retrospective assessments to support prospective designs for future accountability efforts is exemplified for the case of ozone in Text Box 10.2.

Text Box 10.2 Missed Opportunities for Accountability: Ozone Precursor Observations in the Eastern United States

Until the 1990s, little effort was devoted to systematic measurement of VOCs across the United States. Previous to that time canister sampling was performed at various locations on an intermittent basis, and in the United States continuous measurements of non-methane hydrocarbons were attempted after the 1970s. The instrumentation adopted for this purpose proved to be inadequate, so this monitoring was abandoned. The addition of VOC measurements through the PAMS program in the early 1990s partially addressed concerns regarding gaps in ozone precursor observations raised in NRC (1991) and later in NARSTO (2000). The PAMS program deployed improved VOC measurement-technology, but PAMS did not include required improvements in nitrogen oxide measurements. During the PAMS implementation period, a scientific consensus emerged supporting the importance of NO_x in abating ozone levels in certain locations, as conveyed through the NRC study, and apparent earlier success with NO_x reduction in southern California. Air program management strategies were modified to incorporate this new knowledge, and NO_x reductions from major power plant emissions in the Midwest and the East and from mobile sources nationally became the dominant national strategy. This strategy resulted in a downward trend of regional NO_x emissions starting in the late 1990s (Fig. 10.3; also Chap. 12).

Despite over 15 years of lead time, improved measurement of NO_x was not adopted by national monitoring networks. This lack of investment in NO_x observations has precluded thorough measurement-based assessments of the efficiency of the NO_x SIP Call that was implemented in the mid-1990s. Tracking changes in NO_x concentrations offers complementary insights relative to urban-based VOC measurements for assessing the effectiveness of major emission reductions strategies for ozone abatement. Neither measurements of VOC nor NO_x precursor reduction trends combined with ozone changes have been compared in non-attainment areas with early air quality model projections to trace how these projections compared with reality (see also Chap. 7).

Recent partial accountability analyses (EPA 2005; Gégo et al. 2007; and Frost et al. 2006) of the effectiveness the NO_x SIP Call have relied principally on inferential analyses that combine ozone observations with back-trajectory analyses and modeling results to illustrate the apparent success of NO_x reduction efforts (see also Chap. 12). Satellite-derived NO_2 data (Kim et al. 2006, Fig. 10.4) has provided a relevant source of regional ambient nitrogen dioxide concentrations demonstrating the value of this source of observations.

Ideally, a monitoring network for reactive nitrogen (NO_y—which includes most of the gas-phase transformation products of originally emitted as NO_x) in

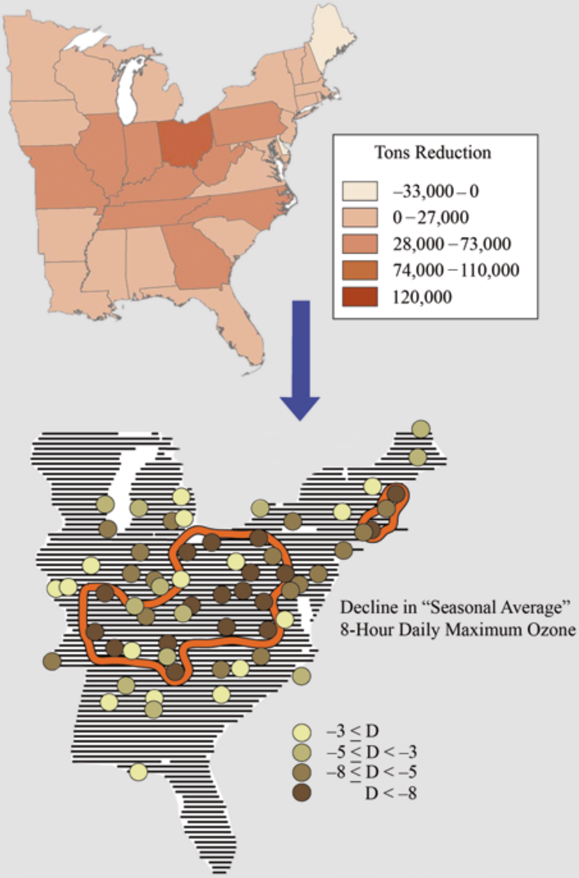

Fig. 10.3 Association between the high ozone season power plant NO_x emission reductions and observed O_3 concentrations for from 2002–2004. An average 1.1% per year regional rate of decline in ozone concentrations between 1997 and 2002 increased to 3.1% per year between 2002 and 2004, the period associated with deployment of NO_x SIP Call reductions. (EPA 2005)

representative sites would have allowed more direct confirmation of expected emissions and ozone responses, as well as improved diagnostic ability to understand potential unexpected outcomes on the regional scale. Ironically, the minimal response of ozone to VOC emission reductions in some locations up to the late 1980s and early 1990s is often cited as an example of how missing key indicators for assessing and diagnosing progress was responsible for a lag in implementing NO_x reductions (Demerjian et al. 1995).

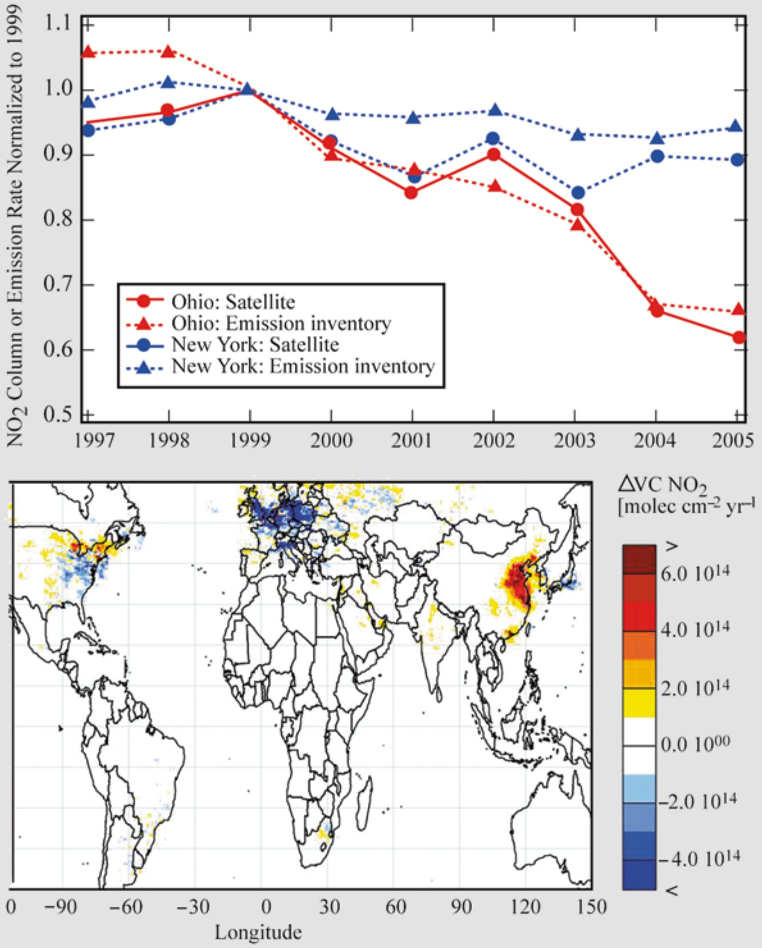

Fig. 10.4 Evidence of reductions in the midwestern U.S. and European NO_x emissions, and increased NO_x generated in eastern Asia (see also Chap. 12). *Top*—superimposed eastern U.S. emission and combined GOME and SCIAMACHY NO_2 1997–2002 trends (Kim et al. 2006); *Bottom*—GOME NO_2 trends from 1995–2002. (After Richter 2005)

As the example in the text box indicates, observations combined with air quality modeling can provide important evidence regarding the effectiveness of air quality control strategies. The analysis described in the text box would have been even more convincing from a multipollutant measurement standpoint if changes in the VOC concentrations over the area analyzed had been documented. A better understanding of the urban reductions in ozone would also have been possible if measurements and methods had been available to differentiate the ozone observations in terms the influence of local versus regional precursor emissions.

10.7 Prospective Measurement Needs

10.7.1 Accountability

The NO_x SIP Call and earlier VOC-focused control efforts in the United States exemplify missed opportunities for assessing the effectiveness of regulatory actions. In the future, projections of the reductions in pollutants expected from projected changes in emissions should be used as a guide for ambient atmospheric monitoring design. Comparisons of estimated actual emission changes with measured ambient concentrations, in the light of the model projections, complete at least part of the risk assessment cycle indicated in Fig. 3.2.

Ambient air monitoring is the crucial element in accountability assessments: Does the system respond as predicted and if not, what modifications to the emission reduction strategies are suggested by the analysis? The kinds of monitoring needed to address this question share elements with current programs, but they can differ from designs that are intended to demonstrate compliance with an ambient standard or goal. The monitoring needed to support accountability can directly support development of an evolving emission control strategy, while also providing better information on population exposure.

Basic considerations to be considered in designing accountability monitoring include identifying:

- Locations of expected high concentration and concentration gradients (or deposition) changes.
- Areas in close proximity to receptors of concern (e.g., high population density, sensitive ecosystems).
- Changes in spatial concentration gradients and temporal trends in precursor or and product concentrations.
- Atmospheric species linked closely with emission signals (e.g., precursor gases and resulting transformed species).
- Specific targeted atmospheric species associated with a standard or goal.
- A baseline reference and extending measurement duration throughout a deployment period of interest.

Given these considerations, a logical starting point for filling monitoring gaps and enabling future accountability assessments is to inventory major emission-reduction initiatives expected to be implemented over the next decade (e.g., Table 8.2). The adequacy of existing monitoring assets for conducting an accountability assessment can then be evaluated in terms of their ability to document, interpret, and understand the anticipated emission and air quality changes. One way to assess the adequacy and feasibility of the monitoring and accountability demonstration plan would be to use air quality modeling (and, possibly, exposure modeling) to estimate the changes in ambient concentrations (and exposure) that would be expected from the anticipated changes in emissions, while taking expected meteorological variability into account. Such analysis should include multipollutant considerations since most emission controls typically impact more than one pollutant and changes in one pollutant, particularly secondary pollutants, can be non-linear and strongly dependent on the presence of other pollutants or chemical intermediates (see Chaps. 7 and 8). Such advanced accountability-based monitoring strategies would need to consider various spatial and temporal scales relevant to determining health and ecosystem responses and include both CPs and HAPs.

The current portfolio of observations of ozone, CO, PM_x mass, NO_y, NO_x, SO_2, VOCs, $PM_{2.5}$ composition together with HAPs, such as mercury, can be applied to address regional and rural coverage and spatial gaps across North America. With application of air quality modeling as described above, observational site locations could be refined for North American management strategy development taking into account source distributions and the range of pollutants of interest.[6]

On much smaller spatial scales, near-source (e.g., near-roadway) concentration gradients are poorly characterized. In 1970–1985, there was a large investment in localized near-field monitoring of large electricity generating units and industrial sites to establish gradients and confirm compliance to standards, but these kinds of studies generally have not been attempted for more diffuse sources like highways, or area sources; and when attempted, they have not been sustained.

The development and deployment of a monitoring system for measuring local scale gradients has to balance limited resources with the introduction of non-routine instrumentation to determine key attributes of neighborhood environments such as near-roadway conditions. As a specific example, continued desulfurization of diesel fuels could reduce particle number concentrations (Wahlin et al. 2001) and new emission controls or engine modifications should reduce NO_x and VOC emissions in near-roadway environments. However, an observation system to track these changes at different representative locations is not in place. These near-field gradient-exposure issues may best be dealt with by a specially designed program of periodic or intermittent measurement over a period of years, taking into account major changes in source technologies (or fuel substitution) in analogy to past intervention studies (see also Chaps. 5 and 12). Mobile measurement platforms (e.g., Sem et al. 1980; Bukowiecki et al. 2002; Kolb et. al. 2004; Polina et al. 2004; Westerdahl et al. 2005; Yli-Tuomi et al. 2005; Xu et al. 2007; Beckerman et al. 2008) can provide a consistent, adaptable means for addressing these needs, including optimization of fixed site placement. Mobile laboratories are becoming more common as a facility for monitoring agencies and current advances in technology are allowing even more-sophisticated measurements to be obtained.

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[6] Exercises for monitoring network design, setting specific goals and using observations and modeling have been done in both urban and regional settings (e.g., California monitoring system, including the Los Angeles area), and studies such as the sulfate regional experiment (Mueller et al. 1982; Hidy 1982) and later the MATEX (e.g., Hidy et al. 1985), The San Joaquin Valley Air Quality Study (Blumenthal and Watson 1994); the SEARCH (Hansen et al. 2003) and the EMEFS experiment. (e.g., Hansen 1989). This approach underlies the idealized NCore design as well (e.g., http://4cleanair.org/Scheffe-Gilroy.pdf [accessed April 2009]).

10.7.2 Accountability and Exposure

Associating concentrations of ambient pollutants with health-effects is a complex problem because, exposure and dose vary with pollutants and human activity. Demonstrating that air quality management actions have had their intended effect on health, for example, will require demonstrating that they have reduced exposure to the pollutants in question. Such a demonstration may require more than just showing that broad-scale ambient concentrations have been reduced.

Advanced exposure assessments employ models that account for human population behavior and pollutant concentrations within the spaces occupied by this population to estimate potential exposures (see Chap. 5). Application of these models requires characterization of fine-scale outdoor concentration patterns relevant to these populations and of the concentrations within the activity-based microenvironments they occupy. Thus, determining exposure and health effects requires models that can extrapolate air quality monitoring data to the spatial and temporal scales required by exposure models. Expanding such approaches to multiple pollutant exposure poses an additional increase in complexity that has not been attempted to date, except in exploratory research designs exemplified by ARIES in Atlanta, SCAMP in Steubenville, Ohio, and BAQS in Windsor, Ontario (Wheeler et al. 2008) and Vancouver, BC (Henderson et al. 2007).

Intervention studies represent another case where improved monitoring would advance our understanding of the effects of air pollution on health and improve our ability to assess the effects of exposure to multiple pollutants. Intervention studies conducted to date have mostly relied on serendipity, where relatively sudden and dramatic reductions in emissions have occurred due to quick implementation of an air quality management policy or an industrial shut-down. Such actions can lead to reductions in concentrations of a group of pollutants (e.g., SO_2 and PM_x plus metals or carbon), although in most cases the details of how the total air pollutant mixture changed have not been tracked (nor have all relevant health measures been accounted for). Thus, analyses of these events have generally accounted for the effects of sudden changes in emissions using an exposure indicator (nearby ambient monitoring data, which is usually limited in scope) and a readily available health-related outcome (e.g., mortality rate or hospital admissions for emergency room visits). While these analyses have been successful in differentiating the influence of pollutant changes on health impacts, which may not be determinable by time series analysis over long periods of time, they have relied on existing local monitoring systems. Thus, information about which pollutants in the typical mixture are responsible for the health benefits is often ambiguous. If intervention studies could be identified ahead of time, a more comprehensive monitoring plan could be adopted which would add value to the study results.

Future intervention opportunities need to be identified in advance, whether they are related to major initiatives like CAIR or CAMR or to changes in fuels, transportation, or other technologies (see also Table 8.2 and discussion in Chap. 8). In this way, measurement programs could be designed and put into place in time to take advantage of the health effects information these opportunities can provide. With such measurements and with appropriate health-related information, considerably more insight could be gained regarding the acute effects of exposure to multiple pollutants, thus providing some of the knowledge needed to move to *Level 3* and *4* multipollutant air quality management approaches.

10.7.3 Multipollutant Measurements Supporting Computer Modeling

Models are used for a number of purposes, ranging from forecasting air quality for public notifications to determining emission reductions needed to meet air quality goals. Multipollutant air quality management will require that closer attention be given to model outputs other than criteria pollutant concentrations. Increased emphasis will need to be placed on the models' fidelity in simulating concentrations and atmospheric processes (to ensure that the model "gets the right answers for the right reasons") for the pollutants of importance as well as for their precursors and reaction products. With these increased expectations, the predictive and interpretative capabilities necessary for management strategies will need to continue to take advantage of the weight-of-evidence for demonstrating accountability and planning feedback (Fig. 3.2). The role of modeling and the complexity of the models can be expected to increase as reconciliation of projected concentration or deposition changes with more detailed observations is used to evaluate and tune air quality management actions.

Tracking a wide range of additional species accounted for in models, including HAPs, will be required. In many cases, attempts to examine a model's reliability in simulating spatial and temporal variations of a collection of pollutants have revealed significant shortcomings (see Chap. 9). Intensive field campaigns have provided observational data sets to address such limitations in support of evolving model development and evaluation. The increased use of models to address the added spatial, temporal and compositional complexities of multipollutant management and the need to evaluate the performance of these models provides one more requirement for multipollutant measurements beyond CPs and HAPs. As pointed out previously, current monitoring networks are not instrumented, sited, or operated for this purpose, except in cases such as the U.S. Supersites program, including its extension in New York, the SEARCH in Atlanta, and recent field intensives in Canada such as Pacific 2001 and BAQS-Met and MILAGRO in Mexico.

Air-quality model development and evaluation relies on observational data typically designed for multiple purposes. Their application for modeling entails a number of incompatibilities between model results, observations, and key observation gaps. These include:

- Limited vertical gradient and atmospheric column observations constraining our knowledge of pollutant transport and formation.
- Inadequate observations in urban areas that can lead to substantial uncertainties in the geographic representation of surface concentration fields or gradients.

- The absence of important chemical process indicators such as nitrogen oxide species—NO_y, HNO_3, HONO, formaldehyde, and free radical species (hydroxyl, hydro- and organic peroxides) leading to unexplained model behavior.
- Uncertainties in predicted dry deposition rates resulting from inadequate spatial and temporal resolution of micrometeorological flux measurements.
- Imprecise representativeness associated with "point" field measurements compared with volume averaged cells of atmospheric chemistry models, including areas of large concentration gradients in urban environments.

Routine air quality surface observations and aloft combined with remote sensing and well-designed intensive field campaigns do provide compositional, temporal, and spatial resolution supporting operational and diagnostic evaluations of model performance (see Chap. 9). These evaluations support continuing development of the models, which will increase in multipollutant complexity depending on the availability of emissions data, and appropriate boundary and initial condition data. The utility of routine monitoring data for evaluating model processes is limited. Routine monitoring networks emphasize the measurement of regulated pollutants using methods and sampling frequencies needed to demonstrate that the relevant standards are being met. Site locations focus mainly on urban areas with sampling heights close to the breathing zones of humans, with measurements in rural locations determined by what is needed to document optical effects and deposition to vulnerable aquatic and terrestrial systems. The more stringent demands of multipollutant air quality management and accountability place a priority on network designs that provide sustained, or at least periodic, high-resolution observations in urban population centers that extend, with a lower spatial resolution requirement, into rural areas and include information on vertical profiles through the boundary layer and into the free troposphere. These networks will need to provide information that allows examination and characterization of the air chemistry of HAPs, as well as a number of other chemical indicators that complement measurements of CPs (see Sect. 10.2 and Chap. 7).

Implementation of the observational system across North America to support risk-based, results-oriented multipollutant air quality management will challenge the data management and modeling communities. As the information needed to estimate exposure (a basic requirement for moving to *Levels 3* or *4* in the multipollutant air quality management continuum) cannot be generated by measurements alone; models will be needed to complement the observations. These models must be sophisticated in their representation of physical and chemical processes, and they will require a nesting of multiple spatial scales to incorporate gradients associated with specific emission sources, meteorological variability, and air chemistry. Meteorological models incorporating four dimensional data assimilation (FDDA) could be adapted for chemical data assimilation (in order to improve the accuracy and resolution of pollutant concentration fields), although the complexities of balancing mass across multiple species poses substantial numerical challenges. An example of merging or "fusion" of model results and observations through computer post-processing is being conducted for the United States from 2001–2005 as part of the joint EPA-CDC Public Health Air Surveillance Evaluation PHASE project (http://www.cdc.gov/nceh/tracking/phase.htm). Similar activities are underway in Canada in support of air quality prediction and have thus far led to "fused" fields of surface ozone across North America (Craig et al. 2008).

Air quality models can also be used to assess the accuracy of emission estimates, especially for dispersed or area-source emissions that must be estimated using emission models. Measurements of ambient concentrations place a constraint on emission estimates. Using inverse modeling (e.g., NARSTO 2005) one can deduce the magnitude and spatial distribution of the emissions that are compatible, according to the model, with the observed concentration field. Initial efforts to assimilate chemical data for air-quality forecasting purposes are expected to evolve toward more widespread integration of observations and models that will facilitate retrospective assessments of emission inventories. Conceptually, the combination of output from observing systems and models will be relied on to provide the detail across environmental media, pollutant classes and spatio-temporal regimes that will be needed for risk- and results-based air quality management. In using such merged products, the uncertainties inherent to both measurement and modeling will have to be recognized and accounted for.

10.8 Improving Future Measurement Programs by Design

As previously noted, resource limitations place a considerable constraint on the kinds of observing systems possible to support the various levels of multipollutant air quality management and accountability. The following sections provide a series of recommendations for improving current observational networks and moving this system towards what is required to support risk-based, results-oriented air quality management. The recommendations are presented in two categories covering planning and design steps and more traditional measurement needs. A priority order is proposed within each category.

10.8.1 Planning for Accountability: Observational Design for Major Air Quality Management Initiatives

A detailed measurement strategy and implementation plan that provides, at a minimum, a demonstration of accountability from changes in emissions to responses in ambient concentration fields should be a required part of any new rule or policy. At present, ambient measurement requirements are specified in promulgation of new standards, with accompanying requirements for an assortment of reference or equivalent techniques. However, with the exception of continuous source emission monitoring for major initiatives (e.g., CAAA Title IV; proposed CAIR; the NO_x

SIP Call; fuel desulfurization in Canada and Mexico), rigorous plans for ambient measurements to quantitatively assess the effectiveness of the implementation of a new rule or policy do not exist. Consequently, without improvements in planning and resource commitments, stakeholders will continue to rely on ad hoc compliance-oriented observations that are not designed to probe the effectiveness of future emission reduction strategies and to explain any observed shortcomings.

The cost of the measurements needed to evaluate the effectiveness of air quality management actions are a small fraction of the cost of implementing controls. Thus, they should be considered a wise investment. Furthermore, a soundly designed measurement program, combined with effects analysis, could provide early information on the effectiveness of the action as implemented, and support midcourse corrections (e.g., interactions shown in Fig. 3.2), if needed.

10.8.2 Multiple Pollutant Networks and Measurement Programs

As discussed previously, future networks supporting risk- and results-based multipollutant air quality management will require advanced designs that take into account evolving criteria and air quality management goals and the limitations of resource constraints. Such thinking has not advanced far beyond the needs to support *Level 1* and *2* air quality management as discussed in Chap. 3. Nevertheless, some preliminary advances in this direction can be seen in recent U.S. ambient air monitoring strategies (Scheffe et al. 2009). As an example, the deployment of the 75 NCore surface stations in the United States (see Text Box 10.3) incorporates a variety of the attributes that would be desired in a multipollutant air quality management network, namely measurements of CO, SO_2 and NO_y co-located with aerosol speciation samplers.

Text Box 10.3 Emerging Multipollutant Monitoring Networks

A new U.S. multiple pollutant monitoring network referred to as the National Core program (NCore) was incorporated into the 2006 revisions to the particulate matter standards (EPA 2006). When implemented in 2009, NCore will provide a minimum of 75 (monitoring) Level 2 sites (Fig. 10.5) in most major urban areas and important transport corridor and background locations, largely benefiting from existing PM speciation network infrastructure. The NCore system will include a variety of trace gas, aerosol mass and speciation measurements of regulatory interest, which are intended to support multiple data user needs (e.g., air quality model evaluation, trends analysis and long term epidemiological studies). While this modest addition of sites will provide some direct diagnostic and community measurements, it is expected that the program will catalyze future growth of multiple pollutant sites. In addition to establishing a multipollutant measurement framework, the NCore sites are intended to provide a backbone of central location sites that can be comple-

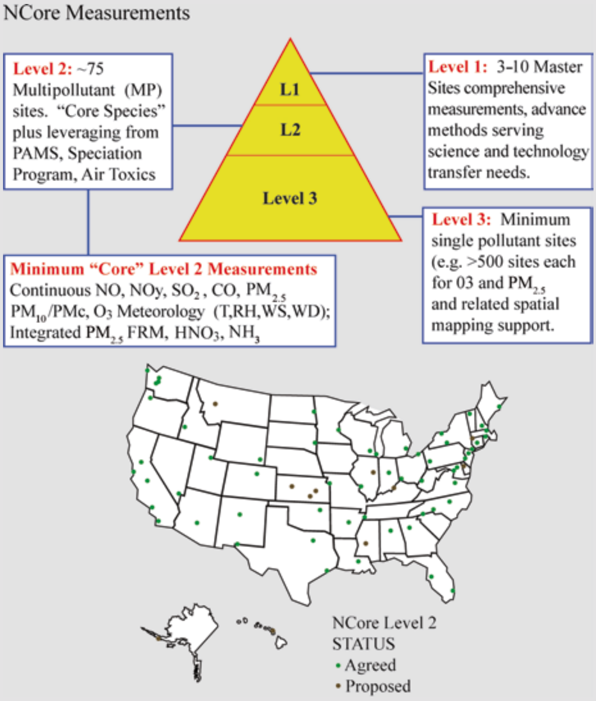

Fig. 10.5 Proposed 3-tiered NCore design (*Top*) and accompanying proposed site locations for Level 2 multiple pollutant sites

mented by additional (existing and new) stations to address more specific spatial resolution requirements.

The NCore air quality species at a minimum include: trace gas level SO_2, CO, NO_y, ozone, NO, gravimetric $PM_{2.5}$ and $PM_{10\text{-}2.5}$, continuous $PM_{2.5}$ and $PM_{10\text{-}2.5}$ mass, speciated $PM_{2.5}$ and $PM_{10\text{-}2.5}$ and ammonia (24 h average on 3 day speciation schedule) through a denuder technique. EPA plans to add true NO_2 to the measurement list, pending development of a reliable, routinely operating sampling and instrumental protocol. A lack of funding support has hindered implementation for more intensive Level 1 sites, intended to promote transition of new technologies into routine networks, which were endorsed by the CASAC monitoring subcommittee.

Among the Canadian NAPS and CAPMoN sites, several sites across the country include the CPs, time-resolved $PM_{2.5}$ mass (TEOM or BAM), $PM_{2.5}$ and $PM_{10\text{-}2.5}$ mass and speciation and VOC speciation, thereby resembling the NCore level 2 sophistication. The most instrumented continuously operating site in Canada is located in Egbert, ON. All the CAPMoN parameters, NO, NO_2, NOy, PAN, plus meteorology and climatological parameters are measured at Egbert. Also operating are filter/denuder samplers for $PM_{2.5}$ and

$PM_{10\text{-}2.5}$ mass and speciation and NH_3 and HNO_3 and canisters for VOCs. A GC/FID system is also operated at Egbert for semi-continuous VOCs measurements. There are a number of remote sensors in operation such as an ozonesonde, DIAL (upper atmosphere), LIDAR, wind sounders, a sun photometer and a Brewer upper atmospheric spectrometer. Egbert is regularly used for specialized field studies in support of methods development and atmospheric chemistry, which includes an on-going intercomparison between CASTNET and CAPMoN. Close to Egbert (~15 km) is "Borden," which is a forested site used for flux research. Short-term intensives are regularly undertaken and long term, continuous energy and CO_2 fluxes are monitored for climate research. The integrated nature of Egbert is further exemplified by the existence of a long-term Smithsonian biodiversity plot.

Since the basic tenets of the NCore program were vetted and approved through EPA's Clean Air Scientific Advisory Committee (CASAC), there are opportunities to leverage this program to improve integration of air quality assessments at a *Level 2* stage of multipollutant air quality management and to be more responsive to accountability needs. Progress can be made to improve multipollutant coverage by carefully considering NCore site locations and species measured. Presently, NCore sites will be located in a mix of urban and rural locations. The list of cities to be included should undergo review to ensure that locations with planned health effects and exposure studies are supported with the most relevant measurements. In some instances, the timing of deployment may need to be adjusted to coincide with the timelines of such studies or with the implementation of certain policies (e.g., to support accountability assessments). Similarly, a subset of rural NCore stations could be located at existing ecosystem study-sites such as ecological research sites in National Parks or experimental forests like Hubbard Brook, NH, or Walker Branch, TN. Highly integrated research sites of this type would form an observational infrastructure supporting bidirectional media-exchange modeling systems and the collection of data extending further along the accountability chain. Furthermore, an effort toward coordinating NCore station siting with other relevant programs would not only improve knowledge of the links between atmospheric stressors and ecosystem responses, but also strengthen the technical basis for advancing multipollutant assessments and accountability. Improved coordination of these interrelated research issues would also increase awareness and application of the measurements within a broader user community.

The NCore parameter list (Text Box 10.3) was developed over several years ago and has been modified to include speciated $PM_{10\text{-}2.5}$. Since that time, heightened interest has emerged for using NCore to study multimedia exchanges, climate-air quality interactions, integration of surface measurements with observations from satellite platforms, and local- to neighborhood-scale assessments. Data requirements for these studies were not factored into the original selection of parameters and site locations. For multipollutant observations, a broadened network capability is envisioned. The following two sections briefly describe a variety of desired measurements reflecting some of these additional needs.

10.8.3 Local Scale and Near Source Exposures

Near-source exposure has become an increasingly important issue in the health science community, as discussed in Chap. 5. An important contemporary example is exposure to roadway traffic emissions. Near-roadway particle and gas concentration gradients are both ubiquitous and markedly different from regional or general urban characteristics that are captured by existing monitoring networks. Given the proximity of significant numbers of people to near-source environments and expected changes in composition associated with introduction of new fuel blends and vehicle technologies, an observational strategy for supporting risk-based multipollutant air quality management should provide repetitive, representative measurements of the spatial gradients associated with significant source classifications to better inform exposure characterization for risk assessment and health effects research. The expense of maintaining fixed sites to examine all such situations of relevance to the North American populations mandates the use of alternative approaches, such as mobile laboratories, that offer opportunities for more flexible sampling. A recent example of such an approach has been demonstrated in Mexico City, as noted in Text Box 10.4, and in ongoing mobile laboratory surveys across major cities in Canada.

Text Box 10.4 An Iterative Short-Term, Spatially-Rich Observation Approach in Mexico City

Complexities in the spatial and temporal structure of pollution as well as chemical and physical composition challenge traditional programs relying on fixed-site monitoring platforms. The challenge is to capture both the complexities in space and properties as well as the longer term perturbations associated with changing source technologies, fuels, climate, and population demographics to address accountability when monitoring resources are limited. While it may be prohibitively expensive to sustain fixed-site routine monitoring of several parameters in multiple locations, periodic campaigns that include consistent measurement designs are a practical approach to meeting this important air quality management challenge. The Mexico City Metropolitan Area (MCMA) campaigns enhanced observed spatial resolution of multiple pollutant patterns through a mobile platform containing high time-resolution and high-sensitivity instruments. In this design, enhanced sampling using a set protocol was conducted for 1-month periods in 2003 and 2006 (Molina et al. 2007, 2008). A relative pattern of pollution behavior was discovered, despite the limitations of having only two observation periods.

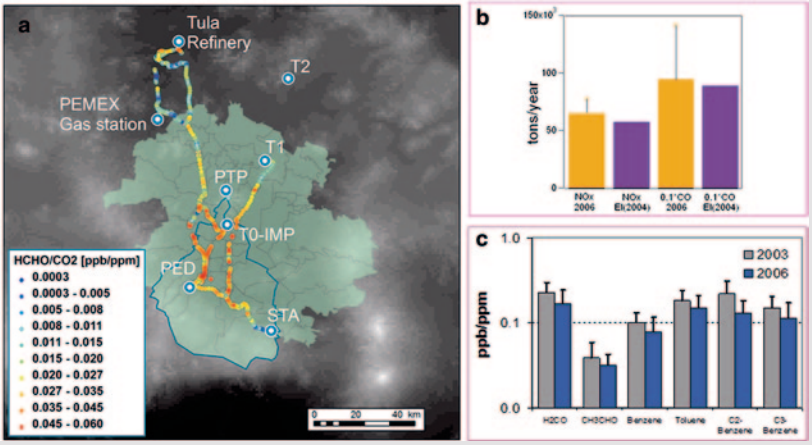

Fig. 10.6 **a** Distribution of formaldehyde in major Mexican City arteries. **b** Estimated changes in NO_x and CO emissions rates. **c** Trends of selected on-road fleet average exhaust VOC emission ratios (ppbv pollutant/ppmv CO_2). (After Zavala et al. 2006, 2009)

Clearly, once such a pattern is established the area can be revisited on a regular schedule or as needed to examine new issues or to follow up on information needs identified in the previous measurement periods (e.g., Fig. 10.6).

Some examples of the type of non-conventional measurement and siting strategies that could serve future needs include:

- Selecting two or more representative sites (operated for multiple years on a regularly scheduled intermittent basis) near roadways to provide better sampling of emissions from in-use vehicles (e.g., determining the preponderance of light duty vs. heavy duty trucks or buses) and account for differences in climatic or altitude conditions as well as for diurnal, weekly or seasonal or annual driving patterns.
- Including as a part of standard monitoring networks a mix of routinely operating instrumentation and sample collection comparable with the existing U.S. National Air Toxics Air Stations (NATTS) measurement suite: e.g., particle mass, composition, light absorption, and VOC HAPs (e.g., benzene, 1, 3-butadiene, toluene, xylenes, and carbonyls)
- Conducting periodic special sampling studies to capture near roadway gradients; e.g., a week or more each in warm and cool seasons annually for a period of several years, including measurement of size-delineated (ultrafine through coarse fractions) aerosol mass and chemical composition, PAN, selected carbonyls, and organic nitrogen compounds and documentation of traffic frequency by time of day, number of light duty vehicles vs. heavy duty trucks, etc.
- Incorporating within the design protocols of monitoring stations the potential to link with ongoing or prospective exposure assessment and health effects cohort or panel studies.

Increased collaboration between atmospheric scientists and the exposure and health science communities should bring new insights into the effects of air pollution and help justify important changes in monitoring design such as those suggested in the enhanced roadway study described above. Multi-disciplinary research activities focused on multipollutant exposures and effects will be essential in moving to *Level 3* and *4* air quality management. In addition to gradient and composition challenges associated with near-source exposures, a modest set of long-term daily $PM_{2.5}$ speciation measurements and improved characterization of ultrafine particles across communities have long been requested. Although regulatory requirements tend to shape network design criteria, sufficient overlaps exist in measurement needs across regulatory, health and atmospheric science communities that would benefit from a thorough collaborative planning approach on measurement designs.

10.9 Toward Optimizing Multipollutant Air Quality Measurements

In Sect. 10.3, pollutants that are not routinely measured but are important for air quality measurement were discussed. Sustained monitoring of these pollutants at a subset of sites, in conjunction with exposure and effects analysis, are important if not essential additions to current routine observations to enable a transition from *Level 1* management approaches to *Level 3* or *4*. A recap of these pollutants and recommendations for measurement strategies is presented in the following subsections.

10.9.1 Nitrogen Species

Improved speciated nitrogen characterization offers the potential to conduct accountability assessments of air quality management actions affecting major electricity generating units and mobile sources. New concerns link 24-h ambient NO_2 concentrations to adverse health effects. It has also been hypothesized that exposure to organo-nitrates, such as PAN and other organo-nitrate species, has adverse consequences for human health. Thus, special studies are needed to characterize these compounds even though they are difficult to measure reliably in ambient air. Finally, nitrogen compounds are also a concern for ecosystems, and linking atmospheric, terrestrial, and aquatic systems provides an important chemical diagnostic for probing air quality and ecological stress.

The lack of routinely operating instruments for continuous measurement of "true" NO_2 has been an issue for nearly two decades (Demerjian 2000). Improved reliable NO_2 determinations should be added to the planned NCore and other networks, as well as selected Canadian and Mexican locations. This effort will require evaluation and eventual commercialization of research-quality instruments preceding field deployment. Deployment of such instruments should complement existing plans for adding total reactive nitrogen measurements to networks. Measurement of other nitrogen oxide compounds (e.g., PAN, HNO_3, HONO, N_2O_5 and $NO_3\cdot$) will need to be conducted by special programs supporting long-term observations.

A lack of observations of ambient ammonia is a problem given the substantial role ammonia plays in the overall nitrogen deposition budget, its role in secondary aerosol formation, and its function as an active acidifier after deposition to terrestrial and aquatic ecosystems. Routine, time-averaged ambient ammonia observations (e.g., using denuder methods) need to be implemented across some of the IMPROVE and CASTNET stations, as well as at key locations in Mexico and at additional locations in Canada. Measurements at monitoring sites should also be enhanced by addition of special sites for characterizing NH_3 gradients near specific sources or regions.

10.9.2 VOCs, Including Carbonyls

Measuring speciated VOC concentrations in urban and rural environments is critical to managing photochemical oxidant and organic particle formation that might pose health risks in their own right. To implement multipollutant air quality management, it will be necessary to implement an improved and sustained program for reliable quantitative measurements of anthropogenic and natural VOCs in North America. Such a program could supersede the PAMS in the United States and strengthen measurement programs in Canada and Mexico.

The deployment of continuous, quantitative measurements of speciated VOCs, including carbonyls, has proven to be only partially successful. A substantial investment in resources will be required to improve the instrumentation, develop advanced quality control and assurance measures, and make them deployable in field applications. Current measurements of VOC species include many of the common HAPs, and monitoring these on a continuous basis is important (see below). These expanded efforts should also include monitoring a subset of organic species in the condensed phase for exploring health impacts and tracing certain unique sources of particles.

Formaldehyde is an important carbonyl involved in air chemistry. It is also a HAP. Consequently, additional effort to obtain spatially and temporally representative measurements of this species is a priority. Improved characterization of formaldehyde serves as a key diagnostic for air quality model behavior, and it is a probable surrogate for biogenic isoprene emissions. Regionally representative formaldehyde observations will also provide an important link to atmospheric column observations provided by satellites. Thus, the addition of a few sampling locations, preferably located at existing or planned multipollutant monitoring stations, would allow development of correlations with observations derived from satellite measurements, potentially enhancing the use of these data in a broad characterization of the spatial patterns of pollution.

10.9.3 Oxidant Speciation

The potential health effects from exposure to the various oxidants present in photochemical smog has been known for some time. In addition to ozone, the oxidants present as peroxides and free radicals should be systematically measured in at least a few urban locations across North America, such as Los Angeles, Toronto, Houston, Atlanta and Mexico City, that experience high photochemical activity. These measurements could be integrated with health-based studies to establish whether the concentration-dose relationships for these oxidants are comparable or potentially more potent than ozone. With such studies, scientists could determine if these species should be incorporated in a risk-based multipollutant air quality management approach.

10.9.4 Hazardous Air Pollutants

The network design and measurement challenges presented by HAPs suggest that greater attention needs to be placed on rethinking monitoring design and instrumentation improvement for groups of pollutants with common origins or chemistry. This rethinking needs to include improved engagement and coordination between health effects and atmospheric science research organizations. While it is argued that integration of HAPs into a multipollutant risk-based management framework (Chaps. 3 and 4) is compromised by a lack of consistent exposure, risk, and benefits metrics, a lack of adequate HAPs observations will delay progress in developing the associations.

It is impractical to design a network for long-term, multi-site measurements of the 187 HAPs listed in the United States, for example. However, the grouping of pollutants by source, chemistry or preferably health-toxicity relationships would serve as a means for creating a measurement strategy that would support multipollutant air quality management at *Level 3* and *4*. This grouping (cf. Chap. 7) could provide a more practical approach for documenting long-term changes in air toxics in key source areas. In this way, the accountability for reduction of air concentrations of key air toxics resulting from emissions management could be tracked more effectively than at present (see also Chap. 12).

10.9.5 Speciated Mercury

A gaseous and particulate mercury measurement network complementing existing observations of mercury in precipitation will afford greater confidence in future mercury assessments. Such a network would foster improved empirical based parameterizations of mercury transformation and removal processes. These measurements are especially important for characterizing mercury chemistry and the more toxic species, methyl mercury, given the scarcity of ambient observations and the difficulty of conducting laboratory-based reaction studies. Mercury pollution embodies most of the features of a fully integrated environmental issue, involving multiple spatial scales of interaction, incorporation of many atmospheric chemistry paths, and feedbacks that occur across and within various media

10.9.6 Design of Measurement and Data Integration Programs

10.9.6.1 Vertical Profiles for Air Chemistry and Meteorology

Addressing air quality over time periods of a day or less, as in some of the stated goals, requires detailed knowledge of meteorological conditions. For weather forecasting, the large-scale meteorological features are well specified daily and hourly by a combination of continuous, routine observations at the ground and aloft. For air quality modeling and analysis, especially at the meso- and finer scale, the required meteorological data can be obtained from these measurements or through specialized data assimilation approaches. However, air chemistry measurements are too limited for reliable forecasting and model applications in many locations, especially in areas susceptible to urban pollution. Knowledge of the vertical distribution of pollutants and precursors is essential for modeling air quality over multiple days. However, vertical profiling of boundary layer and free troposphere air chemistry in North America is limited to specialized field campaigns and a limited number of ozonesonde releases.

Addition of routine boundary layer profiling of basic meteorological parameters (cloud cover, solar radiation, winds, temperature and humidity) and air chemistry would provide enhanced support for model simulations, evaluation, and for emerging efforts to integrate models and measurements, including space-based measurements. Integration is especially relevant as demands increase for improved air quality and deposition characterizations, urban fine-scale analyses for exposure assessment, and for forecasting and accountability. Thus, increased integration of information from multiple sources is expected to be a key technical foundation supporting multipollutant air quality management. Multi-dimensional data (physical and chemical) to support, develop, and evaluate these integrated products are critical to advancing their utility and acceptance.

10.9.6.2 Sentinel Monitoring Stations

Baseline or background levels of criteria pollutants and HAPs are relevant to air quality management in North America because of the potential importance of hemispheric transport. Baseline or background levels are needed for boundary value inputs into air quality models and for assessments of relative risk prepared for the development and evaluation of air quality standards and guidelines. Air quality management and assessment will become more difficult as global backgrounds increase.

Northern hemispheric background concentrations vary spatially and temporally and in some cases they are increasing (e.g., ozone and potentially visibility; Wang et al. 2009). Existing and new candidate locations for North American baseline sites have been identified by the Hemispheric Transport Air Pollution (HTAP, http://www.htap.org/) task force. Existing sites need to be sustained while the global network is expanded to assist intercontinental transport, boundary conditions and background pollution assessments. Moreover, enhancements in continental-scale air quality monitoring and assessment will benefit understanding of the projected interactions between global change phenomena and air quality.

10.9.6.3 Satellite Air Quality Support

The NARSTO (2005) Decadal Study (e.g., Fishman et al. 2008) advocates launching a geostationary tropospheric air chemistry satellite to provide near continuous streams of trace gas and aerosol-related observations across North America. Recent studies using satellite data to characterize large-scale pollution events, identify source regions, and track potential changes in emissions (for NO_2 or particles, for example; also Chap. 11) indicate the value of these data (e.g., Martin 2008; Fishman et al. 2008; Hoff and Christopher 2009). There are growing opportunities to apply long-term satellite observations to the examination of large-scale tropospheric ozone, NO_2, SO_2, CO, HCHO and $PM_{2.5}$ distributions. The interpretation of satellite data in large spatial-scale assessments of boundary layer air quality suggests that development of a multi-organizational, international resource partnership to expand applications of these data to air quality research and management applications would be consistent with European and Asian initiatives.

The use of satellite data is tempered by the recognition that space-based observations typically provide coarse resolution above the Earth's boundary layer and that extrapolating observations to meaningful boundary layer concentrations is constrained by numerous interferences and by the assumptions applied in their interpretation. Consequently, these data must be used with appropriate caution. To facilitate the application of satellite observations to multipollutant management, enhanced cooperative efforts should be fostered between the air pollution management community and the scientists charged with satellite data applications. In addition to plans for the use of data from future geostationary satellite missions, continued progress is needed for processing data streams derived from multi-spectral instruments on existing polar orbiting satellites to better characterize air chemistry in the atmospheric boundary layer.

10.9.7 Information Technology Systems for Data Access and Use

Information technology support, which provides for archiving, accessing, retrieving and harmonizing numerous disparate information sources, is essential for progress in multipollutant management. Efficiently accessing and manipulating emission, observational, and modeling data sets presents significant challenges to users. This requires familiarity with a variety of systems developed independent of one another and having diverse data formatting and metadata reporting standards. Information technology applications to organize, provide access, and integrate data sets will reduce the burden on analysts in understanding and manipulating an increasingly wide range of large data sets is obtained from different programs, including routine air monitoring, meteorological observations, and specialized field campaigns.

Accessibility remains a persistent and unresolved problem. The need to provide adequate data documentation and quality control results in some inherent data access issues. In addition non-uniform database structures adopted by different data managers and various investigators can be problematic. The demands of data processing will increase as the breadth and depth of analyses expand with integration of multipollutant observations and model output. The U.S. system, AIRS for example, is cumbersome to access and use, and access is limited unless individual approval is granted by the data manager. Access to the Canadian system is also limited although an increasing number of data sets is being standardized and made more accessible through the NAtChem archive. Systems like IMPROVE and NADP are easier to access and they are open to investigators via the internet. NARSTO has been archiving data from EPA's Supersite program and from atmospheric chemistry field experiments for a number of years, but this system has proven to be cumbersome for investigators and for some users.

To facilitate interoperability across an integrated hierarchy of data systems, protocols for meta-data descriptions, data formatting conventions, quality assurance, and system interface protocols should be established for individual data supply systems in recognition of the downstream need to integrate with other information sources. The logical form of integration would entail basic sorting and selection criteria based on temporal, spatial and composition attributes that would enable a variety of visual and analytical post-processing tasks. Metadata attributes would include measures of data quality assorted site characteristics, instrumentation and laboratory methods, and sampling frequencies. Revision-control of data sets will also be important. Such conventions would not only increase the use of disparate data sets, but also enable integration of the large data resources across North America. Integrated data systems such as those proposed by the Group on Earth Observations (GEO) offer potential for addressing the information-technology needs of comprehensive assessments, but any emerging system will require a substantial investment and engagement from supporting and user communities. While observational programs continue to generate archives of raw and quality-assured data, increased attention is needed to the North American data system to improve access and manipulation of recorded data in a consistent, long-term oriented format.

10.10 Conclusions and Recommendations

The following are specific conclusions from this chapter:

1. The Canadian and U.S. aerometric measurement system, including air quality and meteorology, is extensive in spatial and temporal coverage. Mexican air quality measurements are limited to the Mexico City area, and some portions of the U.S.-Mexico border regions.
   (a) These measurements are effective for regulatory compliance—the application for which they were designed. However, they are less complete for use in health and ecological exposure-effect assessment or for support of the expansion of new knowledge in the atmospheric sciences.
   (b) The associated networks are focused primarily on population centers and provide support for the existing hierarchy of pollution management regulations and general knowledge about the chemical climate of the troposphere.
2. Long-term measurements of criteria pollutants exist across much of North America, but HAP observations are much more limited both in space and time.
   (a) Human exposure indexes depend on assumed relationships to ambient concentrations. This assumption is likely to remain the driver for ambient monitoring for the foreseeable future.
   (b) Current networks in Canada and the United States are satisfactory for single pollutant *Level 1* and *2* management applications. Mexico is expanding its network beyond Mexico City into other cities, which will be an important addition to continental surveillance.
   (c) Current North American networks are necessary but not sufficient to address multipollutant management at *Levels 3* and *4*, partly because of the lack of measurement of some relevant pollutants, and insufficient resolution to characterize human and ecological exposure
3. Current air monitoring networks are suitable for many determinations of multiscale phenomena in space and time, but they are limited for the extremes of neighborhood and continental-scale phenomena. This limitation is generally alleviated for criteria pollutants by special campaigns, which also support advancing basic knowledge and air quality model development and applications.
4. Today's air monitoring systems generally include some multipollutant information, but they are constrained by certain well-known observational limitations including observations of photochemical oxidants, nitrogen species, volatile organic carbons (including carbonyl compounds), species of particulate organic carbon, and common HAPs (including dry deposition of mercury).
5. Enhancement or redeployment of the current air monitoring systems to accommodate multipollutant management requirements at *Levels 3* and *4*, particularly accountability and relative risk analysis of exposure, will depend on the development of specific management policies evolving from current North American practices.

The following are recommendations for future measurement programs:

1. North American air quality measurement systems should be reviewed in light of competing needs for determining compliance with air quality goals and documentation of trends with emission reductions to aid accountability analysis. Improved spatial and temporal coverage for multiple key pollutant measurements should be considered along with integration of key air toxics into a subset of measurement sites.
2. The needs for tracking reductions in pollutants in response to regulatory initiatives should be included either as time series observations with fixed stations, or with flexible (mobile), regularly scheduled, intermittent observations using tailor-made programs to enhance long-term observations and accountability analysis.
3. To facilitate risk analysis, improved exposure measurements for key multipollutants should be integrated into routine air monitoring designs and supported with specialized studies, as well as integrated into health science initiatives, including consideration of relevant health data.
4. At a minimum, the long-term monitoring of ecological health should be continued in selected areas of ecological vulnerability; improvements in long-term measurements characterizing the health of terrestrial and aquatic systems should be linked with air quality measurements of ecosystem exposure.
5. To improve knowledge of health related exposures[7] and to facilitate model development in the near term, high priority should be given to expansion of systematic observations at selected sites of photochemical oxidants, including reactive nitrogen compounds, to close the reactive nitrogen mass balance; volatile organic compounds; and associated particulate organic speciation.
6. Increased attention also is needed for improving information on the vertical distribution of pollutants on a regular basis.
7. The application of satellite observations to surveillance of certain air quality parameters shows promise for the long-term, and it should be supported with continuous data acquisition.
8. The use of advanced instrumentation should be encouraged to facilitate expanded, efficient multipollutant observations, while providing for appropriate quality controls.

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[7] While the details of combined outdoor, indoor and activity-based measurements are not discussed in this chapter, progress toward development of reliable exposure metrics with ambient observations is needed. Special studies aimed at exposure models will be required to achieve *Levels 3* and *4*, as outlined in Chaps. 3 and 5.

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Chapter 11
Global Change and Air Quality

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World population growth, industrialization, energy demand, and environmental goals are presently driving rapid global change in emissions with complex consequences for climate, air quality, and ecosystems. As North America strives to reduce its pollutant emissions to meet air quality standards, rising emissions in the developing world may increase background pollutant concentrations and offset some of the gains. Climate change can have important impacts on air quality, and in turn air pollutants are recognized to be major climate forcing agents. Policies to mitigate climate change could have important implications for air quality and vice versa. It is becoming increasingly important to view air quality from a global perspective and to integrate air quality and climate stabilization goals in the design of environmental policy. This chapter presents a review and analysis of these issues with the air quality perspective focused on tropospheric ozone, particulate matter (PM), and mercury.

11.1 Intercontinental Pollution

Intercontinental transport of pollution between Asia, North America, and Europe takes place via the prevailing westerly winds. Asian dust events in the western United States provide a vivid image of this intercontinental transport (Fig. 11.1). Satellite observations of dust transport across the Pacific show that sources in Asia can affect U.S. surface sites in less than a week (Husar et al. 2001), although the average transport time is 2–3 weeks (Liu and Mauzerall 2005). Circumpolar transport of pollution around the globe at northern mid-latitudes takes place on a time scale of a month, and meridional mixing of the northern hemisphere requires about three months. Global-scale mixing of the troposphere takes place on a time scale of a year. These time scales can be used to determine the appropriate spatial scope of air quality policy depending on the atmospheric lifetime of the pollutant considered.

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Fig. 11.1 Visibility impairment at Glen Canyon, Arizona, during an Asian dust event on April 16, 2001 (*right photo*) as compared to a clear day (*left photo*). (Source: U.S. EPA (http://www.epa.gov/visibility/program.html). See Fairlie et al. (2007) for a discussion of the April 2001 dust events including evidence that the dust was of Asian origin)

Pollutants with lifetimes of a few days or less do not generally warrant an intercontinental perspective, while pollutants with lifetimes longer than a month are best addressed from that perspective.

Mercury has long been recognized by the scientific community as a global pollutant for which regulation can best be accomplished by a global emissions treaty (Selin 2005). Mercury is mostly emitted in elemental form Hg(0), which is oxidized in the atmosphere to Hg(II) and subsequently deposited. The atmospheric residence time of Hg(0) is on the order of a year (Selin et al. 2007), sufficiently long to allow transport on a global scale. Although local emissions may affect near-source "hot spots" (Dvonch et al. 2005; Keeler et al. 2006), global model simulations indicate that only 20–30% of U.S. mercury deposition originates from North American sources, and that anthropogenic Asian sources contribute a comparable fraction (Seigneur et al. 2004; Travnikov 2005; Selin and Jacob 2008; Selin et al. 2008). Asian emissions of mercury have been rapidly increasing over the past two decades (Wu et al. 2006) while North American emissions have been decreasing (Fig. 11.2).

Intercontinental influence on surface ozone can also be significant. Ozone has a lifetime of days in the continental boundary layer but several weeks in the free troposphere. It is produced in the free troposphere from anthropogenic precursors vented from the source continents, most importantly methane and NO_x (Fiore et al. 2002). Methane has an atmospheric lifetime of 10 years and thus produces ozone on a global scale. Observations at northern mid-latitudes have shown a rising ozone background over the past century (Marenco et al. 1994), and observations in North America show a continuing rise in background ozone in the past few decades (Lin et al. 2000; Jaffe et al. 2003; Jaffe and Ray 2007). These increases can only be partly explained by anthropogenic emissions of NO_x and methane (Wang and Jacob 1998; Fusco and Logan 2003; Lamarque et al. 2005) and could reflect additional factors such as lightning (Mickley et al. 2001), fires (Jaffe et al. 2004) and atmospheric dynamics (Ordonez et al. 2007).

EPA (2003) defines a policy-relevant background (PRB) as the ozone concentration that would be present in U.S. surface air in the absence of North American

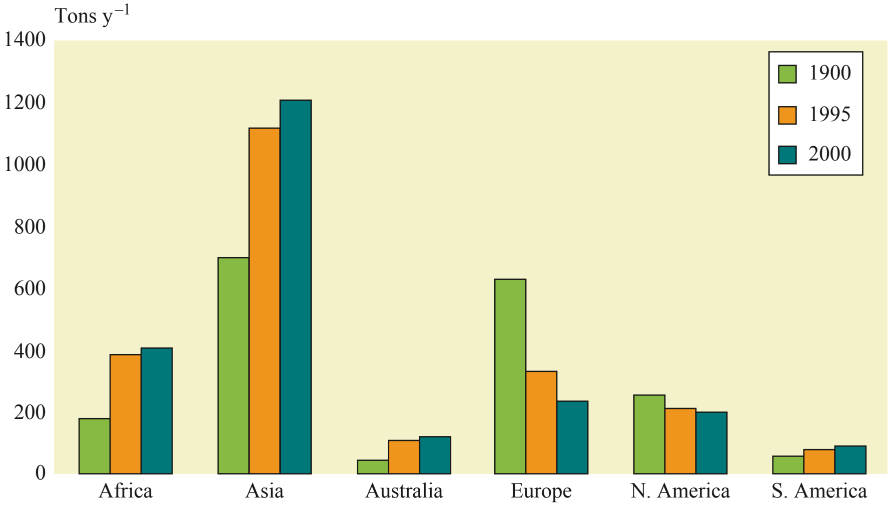


Fig. 11.2 Global trend of mercury anthropogenic emissions by continent, 1990–2000. (Data from Pacyna et al. 2006)

anthropogenic emissions, and thus not amenable to regulation under current policy frameworks. The PRB has been used by EPA as a baseline to quantify the incremental health impacts of North American pollution sources. The present-day PRB is in the range 20–40 ppbv (Fiore et al. 2003), which represents a significant increment toward ozone air quality standards (Fig. 11.3). At least half of this PRB is anthropogenic (Mickley et al. 2001; Shindell and Favulegi 2002; Fiore et al. 2003; Lamarque

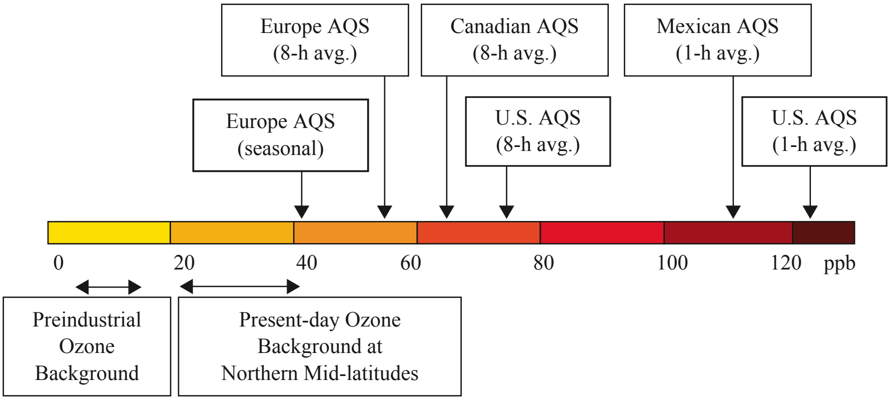


Fig. 11.3 Ozone Air Quality Standards (AQS) and background surface ozone concentrations. The U.S. 8-h AQS was reduced to 75 ppb in 2008. The U.S. EPA is presently (January 2010) considering reducing its 8-h AQS from 75 ppb to a value in the range 60–70 ppb. EPA is also proposing a secondary seasonal standard in a range between 7 and 15 ppm-h (weighted, cumulative exposure to ozone during daylight hours over a three-month growing season) to reduce ozone damage to vegetation

et al. 2005), with a growing contribution from Asia. Asian NO_x emissions have doubled over the past decade and presently enhance surface ozone concentrations in the United States by 3–7 ppbv according to global models (Zhang et al. 2008a). A recent study conducted by the U.S. National Academy of Sciences concludes that the association between short-term changes in ozone concentrations and mortality is generally linear throughout most of the concentration range, although uncertainties make it difficult to determine whether there is a threshold for the association at the lower end of the range. The NRC concludes that if there is a threshold, it is likely to be below the current NAAQS (NRC 2008). Thus, enhancements in ozone concentrations resulting from international transport are implicated in increases in premature mortality rates.

Intercontinental influence on PM is limited by scavenging during transport (Tarrason and Iversen 1998; Park et al. 2004). A major exception is the Arctic in winter–spring, where boundary layer transport of European pollution under dry stratified conditions leads to the phenomenon known as “Arctic haze” (Barrie 1986). Observations and models for the western United States indicate surface air concentrations of Asian sulfate of the order of 0.1 $\mu g\ m^{-3}$ on an annual mean basis (Heald et al. 2006; Park et al. 2006; Liu and Mauzerall 2007; Liu et al. 2008), while van Donkelaar et al. (2008) report 0.13–0.17 $\mu g\ m^{-3}$ for western Canada in spring. These intercontinental pollution enhancements are of little concern for air quality standards, though they could affect visibility standards under the Regional Haze Rule (Park et al. 2006).

In addition to ozone and PM, recent air quality policy has focused on a large number of hazardous air pollutants (HAPs) that can be harmful to human health. The U.S. EPA lists 187 HAPs with atmospheric lifetimes ranging from minutes to years, which determine their potential for intercontinental transport. Most have sufficiently short lifetimes (less than a day) that intercontinental transport is not an issue.

11.2 Effects of Climate Change on Air Quality

Air quality is highly sensitive to weather, and it follows that a change in climate (i.e., in the long-term statistics of weather) may have important air quality implications. Jacob and Winner (2009) give a recent review. Major heat waves in the eastern United States in 1988 and in Europe in 2003 were associated with intense pollution episodes (Lin et al. 2001; Guerova and Jones 2007). Such heat waves are likely to become more frequent in the future climate (Christensen et al. 2007). Interest in the effect of climate change on U.S. air quality has grown in recent years, including in particular through the EPA Global Change Research Program. In Mexico, there are particular concerns about the effects of drought-related forest fires on air quality and whether or not the frequency of severe droughts might be enhanced by climate change. The effect of forest fires on urban air quality in Mexico can be substantial. For example, in the spring of 2005 metropolitan Guadalajara experienced one of the most severe air quality episodes in its history due to a fire in the La Primavera forest (INE-SEMARNAT 2006a).

11.2.1 Twenty-First Century Climate Change

Increasing greenhouse gas concentrations over the twenty-first century are expected to drive significant climate change. Current projections draw mainly from four socioeconomic scenarios constructed by the Special Report on Emission Scenarios (SRES) of the IPCC (SRES 2001): A1 (rapid economic growth and efficient introduction of new technologies), A2 (very heterogeneous world with sluggish economic growth), B1 (convergent world with rapid introduction of clean and efficient technologies), and B2 (focus on sustainability, intermediate economic development). The A1 scenario further distinguishes three sub-scenarios (A1FI, fossil intensive; A1T, predominantly non-fossil; and A1B, balanced across energy sources) by technological emphasis. SRES (2001) reports emission projections for greenhouse and other gases developed by a number of economic models for the different scenarios. The IPCC (2001) reports the multi-model means, and these are the standard greenhouse emission scenarios used in global climate models. The IPCC also includes consistent future scenarios for aerosol and ozone precursor emissions, but these are generally not used in future-climate projections because of the difficulty of converting them into future perturbations to concentrations and radiative budgets. These issues are discussed in Sect. 11.4.

The global climate models (GCMs) used in projections of twenty-first century climate change simulate the climate of the Earth by solving the primitive equations for atmospheric dynamics and physics on a global scale, generally including some coupling with ocean and land dynamics. The IPCC (Christensen et al. 2007; Meehl et al. 2007) reports climate change projections for the twenty-first century from a large ensemble of GCMs applied to the SRES scenarios. The projected 1990–2050 increases in global mean surface temperatures range from 0.8 to 2.7°C for the different GCMs and scenarios. Associated with this projected global temperature increase is a global increase in humidity, due to enhanced evaporation from the oceans, and consequently an increase in global precipitation though with large regional variations. For North America, the ensemble of models projects higher-than-average surface warming, an increase in heat waves, and a wetter climate in the north vs. drier in the south (Fig. 11.4). The results in Fig. 11.4 are for the IPCC A1B scenario in 2090 but similar patterns of change are found for other scenarios and shorter time horizons (Christensen et al. 2007).

11.2.2 Effects of Climate Change on Ventilation

Air pollution episodes are associated in general with suppressed horizontal and vertical mixing, i.e., stagnant conditions and shallow mixing depths. A major factor determining regional stagnation in the East is the frequency of mid-latitude cyclones tracking across southern Canada. The cold fronts associated with these cyclones sweep the polluted air ahead of the front, replacing it with cleaner polar air (Cooper et al. 2001; Li et al. 2005). GCM simulations by Mickley et al. (2004a), Murazaki and Hess (2006), and Wu et al. (2008a) indicate a higher frequency of summer pol-

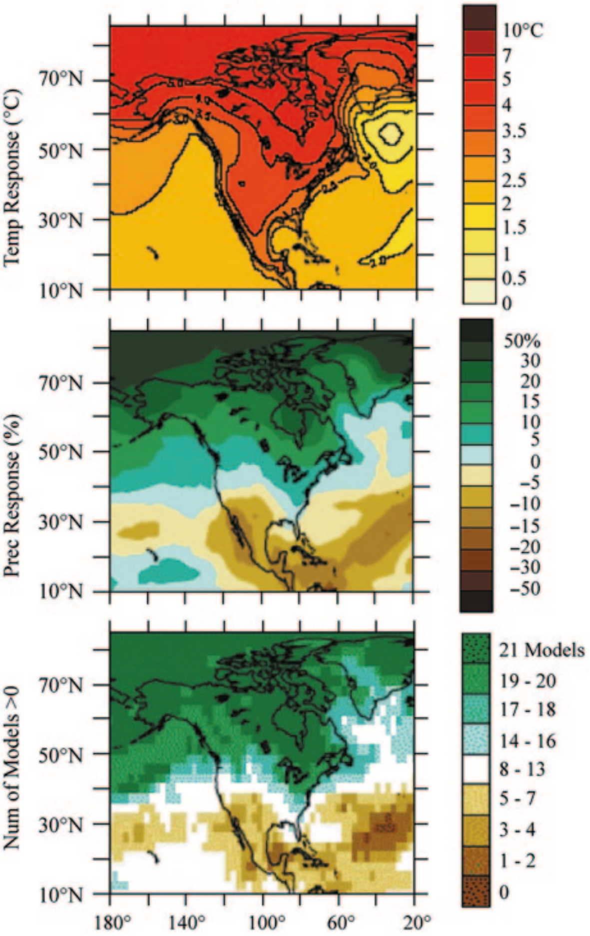


Fig. 11.4 Projected 1990–2090 changes in annual mean surface temperature (*top*) and precipitation (*middle*) for North America (A1B scenario). Values are averages from 21 GCMs contributing to the IPCC (Christensen et al. 2007). The bottom panel shows the number of models projecting a precipitation increase: a value of 21 indicates consensus for an increase, and zero indicates consensus for a decrease. A mid-range value (8–13) indicates lack of consensus regarding the sign of the precipitation change. Model results for other scenarios and shorter time horizons show similar patterns of change. (Christensen et al. 2007)

lution episodes in the central and eastern United States in the future climate due to reduced frequency and northward shift of mid-latitude cyclones. Such a trend in cyclone activity is a robust feature of GCMs at least in winter (Lambert and Fyfe 2006), and can be explained by weakening of the meridional thermal gradient due to strong Arctic warming. Observations for the past several decades show indeed a significant decrease in mid-latitude cyclone frequency (McCabe et al. 2001).

Climate change may either increase or decrease mixing depths, depending in particular on the change in soil moisture. GCM simulations for the twenty-first century climate find inconsistent results (Jacob and Winner 2009). According to Jazcilevich et al. (2000, 2003a, b, 2005), rapid urbanization and its associated land-use changes have had a large effect on mixing depths and urban-scale circulations affecting air quality in Mexico City.

Uncertainty in GCM projections of future climate change generally increases as the spatial scale of interest decreases and as coupling to the hydrological cycle becomes involved. There is a strong need to assess GCM skill in simulating present-day climatological statistics relevant to air quality including mixing depths, stagnation events, and precipitation frequency. Eventually, the multi-model ensemble approach used by the IPCC to assess robustness in projections of future regional climate change (Christensen et al. 2007) should be extended to meteorological variables of interest for air quality. Dynamical downscaling of GCM fields using regional climate models could significantly improve the simulation of air quality (Gustafson and Leung 2007).

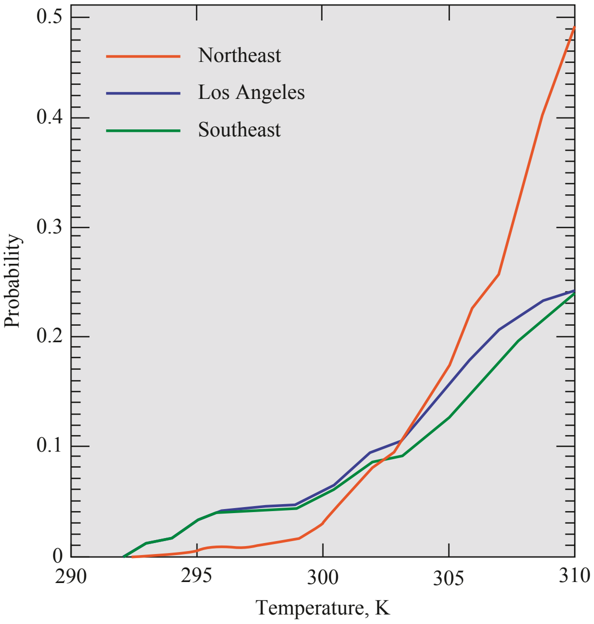
11.2.3 Effects on Ozone

Surface ozone is strongly correlated with temperature during pollution episodes (Jacob and Winner 2009). This relationship is driven in part by the joint association of high ozone and temperature with stagnation episodes, in part by the temperature dependence of emission of biogenic isoprene (a major ozone precursor), and in part by the temperature dependence of the chemistry for ozone formation (Jacob et al. 1993; Sillman and Samson 1995). A few studies have used observed correlations of high-ozone events (>80 ppbv) with meteorological variables, together with regionally downscaled GCM projections of these meteorological variables, to infer the effect of twenty-first century climate change on air quality if emissions were to remain constant. A major assumption is that the observed present-day correlations, based on short-term variability of meteorological variables, are relevant to the longer-term effect of climate change. Cheng et al. (2007) correlates ozone levels at four Canadian cities with different synoptic weather types, and use projected changes in the frequency of these weather types (in particular more frequent stagnation) to infer an increase in the frequency of high-ozone events by 50% in the 2050s and 80% in the 2080s. Lin et al. (2007) apply the relationship of Fig. 11.5 for the northeastern United States to infer a 10–30% increase in the frequency of high-ozone events by the 2020s and a doubling by 2050. Wise (2009) projects a quadrupling in the frequency of high-ozone events in Tucson, Arizona by the end of the twenty-first century.

A number of recent studies have presented a more fundamental approach to the problem by using future-climate GCM simulations, sometimes nested with regional meteorological models (e.g., Leung and Gustafson 2005), to drive global and regional chemical transport models (CTMs), keeping anthropogenic emissions at present levels (Hogrefe et al. 2004; Murazaki and Hess 2006; Racherla and Adams 2006; Tagaris et al. 2007; Tao et al. 2007; Wu et al. 2008a; Lin et al. 2008; Zhang et al. 2008b). Other studies have perturbed individual meteorological variables in CTM simulations for the present climate and diagnosed the ozone response (Steiner et al. 2006; Dawson et al. 2007a).

A general result across all models is that twenty-first century warming is projected to increase surface ozone in polluted regions of the United States and that temperature is the principal driving factor. Increases in the summertime maximum

Fig. 11.5 Probability that the daily maximum 8-h average ozone will exceed 84 ppb for a given daily maximum temperature, based on 1980–1998 data. Values are shown for the Northeast, the Los Angeles Basin, and the Southeast. (From Lin et al. 2001)



8-hour daily average (MDA8) surface ozone are typically 1–10 ppbv depending on the model, the region, and the time horizon considered (Jacob and Winner 2009; EPA 2009). Decreases are mostly confined to clean and coastal areas where ozone is largely determined by its background, which declines in the future climate because of increasing water vapor stimulating ozone chemical loss (Wu et al. 2008b; Lin et al. 2008). Significant increases of ozone in the northeastern United States are found in all models, but beyond this there are large regional differences between models (Jacob and Winner 2009). For example, Racherla and Adams (2006) and Tao et al. (2007) find a maximum effect in the Southeast, where Wu et al. (2008a) find little effect. This difference appears to reflect at least in part different assumptions regarding the fate of isoprene nitrates (Wu et al. 2008a; Horowitz et al. 2007).

A prevailing finding among models is that the ozone increase from climate change is largest under conditions where present-day ozone is already high. Bell et al. (2007) (using model results from Hogrefe et al. 2004) find a strong correlation between present-day ozone and the magnitude of ozone increase for 50 cities in the eastern United States, and attribute it to the higher ozone production potential in areas with high anthropogenic emissions. Jacobson (2008) finds greatest sensitivity in Los Angeles and attributes it to increased chemical sensitivity of ozone to temperature when ozone is high.

Although current emission control strategies will likely remain effective in the future climate (Liao et al. 2007), stronger emission controls may be required to meet a given air quality objective (Wu et al. 2008a). This ‘climate change penalty’ is illustrated in Fig. 11.6 with simulated probability distributions of summertime ozone in the Midwest for 2050 vs. 2000 conditions. We see that the same ozone air

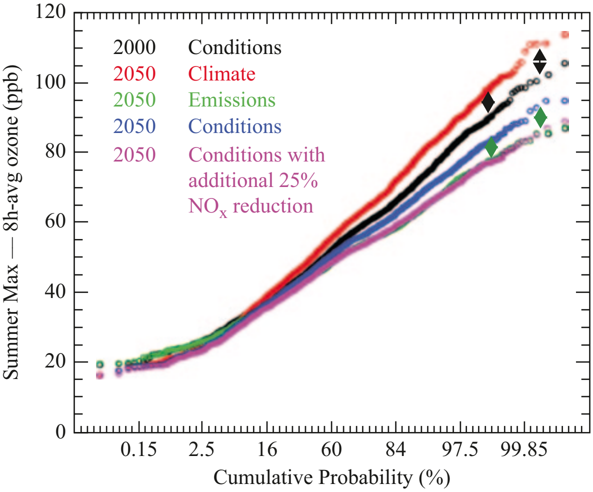


Fig. 11.6 Simulated effect of 2000–2050 global change in emissions and climate (A1 scenario) on surface ozone in the Midwest, illustrating the climate change penalty (Wu et al. 2008a). The figure shows cumulative probability distributions of summer daily maximum 8 h-average surface ozone for (1) 2000 climate and anthropogenic emissions (*black*), (2) 2050 climate and 2000 anthropogenic emissions (*red*), (3) 2000 climate and 2050 anthropogenic emissions (*green*), (4) 2050 climate and anthropogenic emissions (*blue*), and (5) 2050 climate and anthropogenic emissions but with 25% additional domestic NO_x emission reductions (U.S. anthropogenic NO_x emissions reduced by 50% instead of 40% compared to 2000 levels) (*pink*, closely overlaps the *green*). The *black* and *green arrows* measure the climate change penalty for ozone air quality with 2000 and 2050 anthropogenic emissions respectively

quality that would be achieved with a 40% decrease of anthropogenic NO_x emissions for the present-day climate would require a 50% decrease in the 2050 climate. Wu et al. (2008a) find that as U.S. NO_x emissions decrease, the climate penalty also decreases and can even become a climate benefit, thus amplifying the effectiveness of emission controls.

11.2.4 Effects on PM

Unlike for ozone, no strong and consistent correlation is observed between PM concentrations and meteorological variables that would provide guidance on the expected effects of climate change. This is likely because PM includes a number of components with different and complex sensitivities to the meteorological environment. For example, increasing temperature would cause nitrate to decrease but sulfate to increase (Aw and Kleeman 2003; Dawson et al. 2007b; Tagaris et al. 2007). The effect on secondary organic aerosol (SOA) involves compensating factors between increased biogenic VOC emissions and increased volatility (Liao et al.

2007). PM should correlate with precipitation (Dawson et al. 2007b), reflecting removal by wet scavenging, but finding this correlation in the observations is elusive (Woods et al. 2007), possibly because precipitation is in general associated with air mass changes. The few CTM studies in the literature reviewed by Jacob and Winner (2009) indicate ±0.1–1 μg m^{-3} changes in surface $PM_{2.5}$ concentrations in the United States as a result of 2000–2050 climate change, although the patterns of these changes are inconsistent among the various studies.

Climate-driven changes in natural emissions from dust and forest fires could be the most important factors driving changes in PM concentrations. Wildfires in North America have increased over the past decade, reflecting both the legacy of fire suppression in the twentieth century and the effect of climate change (Westerling et al. 2006). Spracklen et al. (2009) project a 50% increase in fire emissions in North America in the 2050 climate solely due to climate change, resulting in a 10% increase in annual mean $PM_{2.5}$ in the western United States.

11.2.5 Effects on Hazardous Air Pollutants

Many HAPs are produced or consumed in the atmosphere by reaction with the hydroxyl radical (OH). Concentrations of OH are generally expected to increase in the future climate due to increase in water vapor (Johnson et al. 1999), but the effect as found in different models is only on the order of 10% over the course of the twenty-first century (Wu et al. 2008b). It is likely that climate-driven changes in pollutant ventilation (Sect. 11.2.2) will affect HAP concentrations more than changes in chemistry.

11.2.6 Effects on Atmospheric Deposition and Mercury

The only study so far to have examined the effect of climate change on atmospheric deposition in North America is the regional climate simulation of Zhang et al. (2008b). They find varying spatial patterns of increases and decreases, reflecting calculated changes in precipitation patterns and regional circulations, as found also in a model study for Europe by Langner et al. (2005). Predicting these regional-scale changes is subject to large uncertainty, as pointed out above. Regardless of changes in the deposition patterns, the total amount deposited is determined to first-order by the amount emitted (what goes up must come down). In the case of acid and nitrogen deposition, the relevant emissions are mainly anthropogenic, and changes in these emissions (Sect. 11.4) would be the main drivers of changes in deposition.

The effect of climate change on mercury cycling through the atmosphere has received little attention so far. A potentially important issue is the volatility of mercury accumulated in land and ocean reservoirs (Jacob and Winner 2009). Volatilization of soil mercury as a result of climate change could be of considerable importance, as the amount of mercury stocked in soil (1.2×10^6 Mg) dwarfs that in the atmosphere (6×10^3 Mg) and in the ocean (4×10^4 Mg) (Selin et al. 2008). Soil mercury is mainly bound to organic matter, and future warming at boreal latitudes could release large amounts of this organic matter to the atmosphere as CO_2 either through increased respiration or through increased fires. The soil mercury bound to this carbon could volatilize to the atmosphere, eventually re-depositing to ecosystems in a mobile and more toxic form.

11.3 Effects of Air Pollutants on Climate Change

Tropospheric ozone and PM are recognized by the IPCC as important agents of climate change (Forster et al. 2007); thus, it follows that air quality policy could have significant climate consequences (Levy et al. 2008a, b). Decreases of ozone and BC PM can mitigate warming, while decreases of sulfate, nitrate, and OC PM can exacerbate warming. The list of climate-relevant air pollutants should also include methane, which is the second most important anthropogenic greenhouse gas and also affects air quality by increasing the tropospheric ozone background (West and Fiore 2005).

11.3.1 Radiative Forcing

The global energy budget of the Earth is determined by a balance at the top of the atmosphere between incoming solar radiation (peaking in the visible), reflected solar radiation, and outgoing terrestrial radiation (peaking in the infrared). Climate is in equilibrium when the absorbed solar radiation (incoming minus reflected) equals the outgoing terrestrial radiation. A change in atmospheric composition can perturb this balance. The radiative forcing associated with this change is defined as the resulting energy flux imbalance at the top of the atmosphere, as computed by a radiative transfer model with all other factors (including temperature) kept at their original equilibrium values. Eventually the climate responds to the forcing by moving to a new energy-flux equilibrium, with associated changes in temperature and other variables.

Radiative forcing has been the standard metric used by the IPCC since 1990 to quantify the contributions of different agents to climate change. It is much easier to calculate than the climate response, and it is more certain because it avoids the complexity of climate feedbacks represented in different manners in different GCMs. The change in global equilibrium surface temperature (T_o) from a given radiative forcing varies by a factor of four between state-of-science GCMs (NRC 2005), but a consistent finding across GCMs is that the response of T_o is proportional to the magnitude of the forcing and largely insensitive to the nature of the forcing agent (Boer and Yu 2003; NRC 2005). This makes radiative forcing a valuable metric to compare the importance of different climate change agents and to develop policies for mitigating climate change.

Radiative forcing is defined as positive if it results in a gain of energy for the Earth system, negative if it results in a loss. Positive forcing causes warming, negative forcing causes cooling. Greenhouse gases including ozone and methane absorb infrared radiation emitted from the Earth's surface and re-emit it at a lower temperature, thus decreasing the outgoing radiation flux and producing a positive forcing. Ozone also absorbs solar radiation in the near-UV and this makes an additional small positive forcing. PM interacts with solar radiation, scattering it back to space (negative forcing) or absorbing it (positive forcing). The absorbing component of PM radiative forcing is mainly BC, and the scattering component is mostly sulfate.

Figure 11.7 from the IPCC (Forster et al. 2007) shows the present-day global radiative forcings from different anthropogenic emissions relative to pre-industrial radiative equilibrium (1750 climate). Figure 11.7 departs from the usual presentation of radiative forcings in that it is based on anthropogenic emissions rather than changes in concentrations. The emission-based perspective (Shindell et al. 2005) is more useful for analyzing the impacts of air quality policy. In particular, the radiative forcing from tropospheric ozone is not identified *per se* but rather as the radiative forcings from the emissions of its precursors, which affect not only ozone but other climate agents as well.

We see from Fig. 11.7 that the largest positive radiative forcing is from CO_2 emissions (+1.56 W m^{-2}). Second is from methane emissions (+0.66 W m^{-2}), representing the sum of effects of methane emissions on the concentrations of methane, ozone, stratospheric water vapor, and CO_2. Third is from BC emissions (+0.46 W m^{-2}), including the effects on both atmospheric concentrations and snow albedo. Anthropogenic emissions of CO and non-methane volatile organic compounds (VOCs) also have significant positive radiative forcings (+0.20 and +0.09 W m^{-2} respectively), even though they are not significant greenhouse gases themselves, because of their effects on OH concentrations (and hence on the lifetime of methane), tropospheric ozone, and CO_2. Adding up the effects of these four emissions relevant to air quality (methane, BC, CO, VOCs) yields a total radiative forcing of +1.41 W m^{-2}, comparable to that from CO_2. Clearly, air quality policy can play a role in mitigating or enhancing climate change over the near term.

Emissions of NO_x appear to have compensating effects on climate (Fuglesvedt et al. 1999; Wild et al. 2001; West et al. 2007). They provide a source of tropospheric ozone (positive forcing) but also of nitrate aerosols (negative forcing), and in addition increase the concentration of OH and hence the loss of methane (negative forcing). The net overall effect in Fig. 11.7 is a small negative forcing (−0.11 W m^{-2}), but the sign is within the range of uncertainty on the individual terms and Forster et al. (2007) decline to give a best estimate.

Anthropogenic emissions of scattering PM have large negative radiative forcings. These include a direct effect from aerosol scattering of solar radiation and an indirect effect from perturbation to cloud properties, the latter being highly uncertain (NRC 2005). Figure 11.7 gives best estimates for direct forcings of −0.40 W m^{-2} from SO_2 emissions, −0.20 W m^{-2} from OC emissions, and −0.10 W m^{-2} from anthropogenic dust emissions (desertification, agricultural erosion). The sources of OC are not well known, and could include a major contribution from SOA produc-

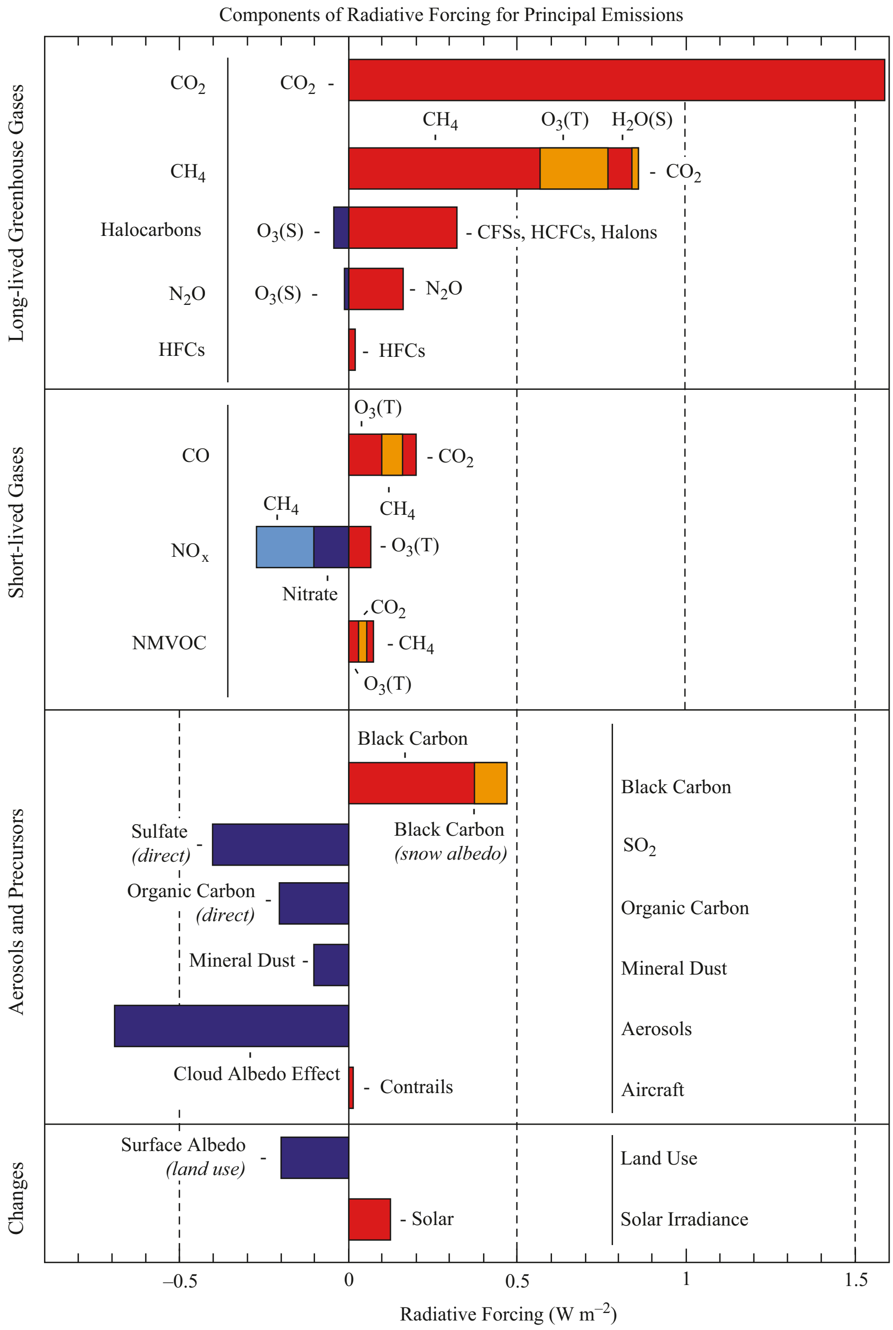


Fig. 11.7 Global radiative forcings due to emission changes between 1750 and 2000, from IPCC (Forster et al. 2007). In the figure, NMVOC refers to (non-methane) volatile organic compounds

tion by anthropogenic VOC emissions not included in Fig. 11.7 (Volkamer et al. 2005; Donahue et al. 2006; Fu et al. 2008). If so, the net radiative forcing from anthropogenic VOCs could possibly be negative rather than positive. The current best estimate of the indirect aerosol forcing given in Fig. 11.7 (−0.9 W m^{-2}) is larger than the direct forcing. Adding up the PM-related negative radiative forcings in Fig. 11.7 yields a total of −1.6 W m^{-2}, indicating that PM may have masked much of the greenhouse warming over the past century. Regulatory actions to reduce emissions of SO_2 will reduce sulfate aerosol concentrations and hence also reduce negative radiative forcing. Air quality policies aimed at PM reductions could thus impede efforts to curb anthropogenic climate change (Ming et al. 2005).

The radiative forcing estimates reported by the IPCC are global averages. Ozone and PM have short lifetimes and hence their radiative forcings show far more spatial variability than those of long-lived greenhouse gases such as CO_2 and methane. For ozone, the spatial gradient in forcing is mainly between the northern and southern hemispheres (Mickley et al. 2004b). For PM, the forcing is concentrated over the polluted continents, and in urban areas of the United States it can reach values of −30 W m^{-2} (Jin et al. 2005). Deposition of BC to snow further contributes a positive regional radiative forcing (Hansen and Nazarenko 2004; Qian et al. 2009). Such regional structure in radiative forcing cannot be simply translated into a surface temperature change because of horizontal transport of heat (Boer and Yu 2003; Levy et al. 2008a). GCM simulations of climate response are necessary for quantitative interpretation and we discuss those next.

11.3.2 Climate Response for North America

Recent model results using the IPCC A1B scenario to examine the effect of changing concentrations of ozone, BC, OC, and sulfate on future climate find that by the year 2100 the projected decrease in sulfate aerosol (driven by a 65% reduction in global sulfur dioxide emissions) and the projected increase in BC aerosol (driven by a 100% increase in its global emissions) contribute a significant portion of the simulated A1B surface air warming relative to the year 2000: 0.4°C globally, 0.6°C (Northern Hemisphere), 1.5–3°C (wintertime Arctic), and 1.5–2°C (~40% of the total) in the summertime United States (Levy et al. 2008a, b).

Mickley et al. (2004b) find that the predicted surface warming from anthropogenic tropospheric ozone is twice as large in the northern as in the southern hemisphere, reflecting the northern dominance of the forcing. They and Shindell et al. (2006) find disproportionately strong warming in continental interiors of northern mid-latitudes in summer, when ozone is highest, in contrast to forcing by CO_2 for which the strongest warming is in winter. Shindell et al. (2006) further point out that the Arctic, where warming has been strongest over the past decades, is particularly sensitive to ozone radiative forcing.

Direct radiative forcing by PM is more localized over source regions than that of ozone, although Levy et al. (2008a) find that the climate response is not necessarily enhanced over the region of forcing but is mostly spread over the global scale. The sharp distinction in temperature effects between PM types is of concern because sulfate in North America has been decreasing faster than BC PM, and this is apparent in some long-term observed trends of radiative forcing (Liepert and Tegen 2002).

Besides this direct radiative forcing effect, PM affects the formation and microphysics of clouds and thus can modify precipitation locally, as has been observed for orographic precipitation (Jirak and Cotton 2006; Rosenfeld and Givati 2006). A climatological data analysis for coastal areas of the western North Atlantic by Ceverny and Balling (1998) shows precipitation to be highest on Saturdays and minimum early in the week, which the authors attribute to precipitation enhancement by anthropogenic PM accumulating over the course of the working week. Forster and Solomon (2003) similarly find a weekly variation in the diurnal temperature range over the United States which they attribute to the effect of anthropogenic PM on clouds. The sign of the effect varies with location, suggesting that PM could enhance cloud formation in some areas and suppress it in others. Bell et al. (2008) find a midweek maximum in summer afternoon rain intensity and storm height in the U.S. Southeast that they attribute to the weekly cycle of PM concentrations.

PM may elicit further climatic responses. A regional model study by Qian et al. (2009) indicates that BC deposition to the snowpack of the western United States has significant consequences on wintertime snowpack accumulation and spring runoff. Jacobson and Kaufman (2006) find a reduction in wind speed over California correlated with anthropogenic PM, which they interpret with a GCM as driven by increased atmospheric stability from PM radiative forcing. PM-driven changes in precipitation and atmospheric stability would in turn affect PM concentrations, representing a possible regional feedback between climate change and air quality.

Regional climate effects of air-quality related emissions can be especially significant in megacities such as Mexico City. Emissions in Mexico City differ substantially from cities in Canada and the United States, with a much higher contribution of carbonaceous PM (Molina and Molina 2002). Magaña (2007) estimates that average temperatures in Mexico City have risen 4–5°C over the past 100 years, which presumably reflects in part the urban heat island effect (Jáuregui and Luyando 1998), in part global climate change, but also the effect of BC emissions. In 2006, two field campaigns (MILAGRO and MAX-Mex, http://www.eol.ucar.edu/projects/milagro/) were conducted in the Mexico City region to characterize emissions from Mexico City and examine their effects on regional and global climate. As results from these campaigns are analyzed, the contributions of local emissions to urban climate change in Mexico City should become clearer.

11.4 Projections of Future Anthropogenic Emissions

The Special Report on Emission Scenarios (SRES) of the IPCC in 2000 included consistent 2000–2100 projections of global methane, CO, NO_x, SO_2 and VOC anthropogenic emissions along with CO_2 for the different socioeconomic scenarios described in Sect. 11.2.1 (Nakicenovic et al. 2000). They do not include consideration of how climate change may affect emissions. Figure 11.8 shows the projections for NO_x, methane and SO_2. All scenarios project a steady global increase of NO_x emissions over the 2000–2050 period, ranging from 20 (B1) to 200% (A1F), and mostly driven by China and India. NO_x emissions in the United States are projected to decrease over that period in all scenarios except A2. Methane emissions are projected to increase in all scenarios. In the A1F and A2 scenarios these emis-

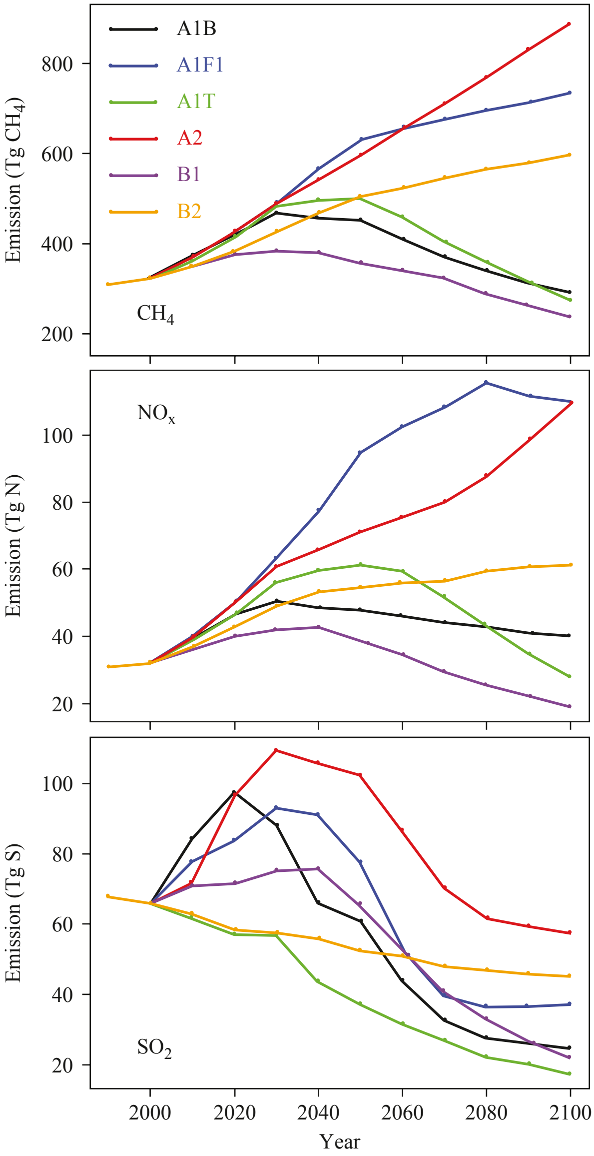


Fig. 11.8 Global 2000–2100 trends of methane, NO_x, and SO_2, for different IPCC SRES scenarios (Source: Nakicenovic et al. 2000)

sions increase by as much as a factor of two by 2050 due to increases in livestock, landfill, and fossil fuel sources. CTM simulations based on the different SRES scenarios indicate that the global rises in NO_x and methane emissions will increase the surface background ozone in the northern hemisphere by 2–7 ppbv by 2030 (Prather et al. 2003; Unger et al. 2006), independent of any climate change.

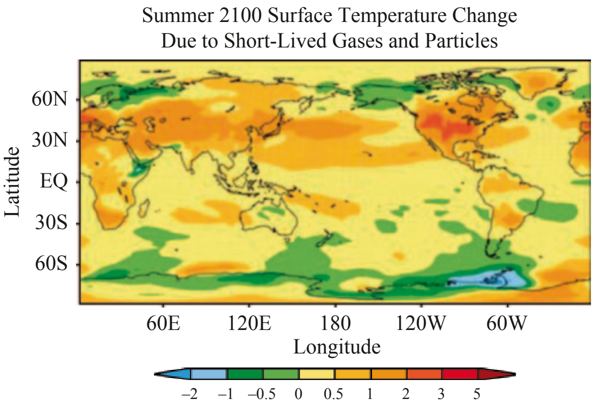
Dentener et al. (2005) suggest that the SRES projections for NO_x may be too pessimistic because they do not sufficiently account for recent and pending air pollution control legislation in the developing world. The authors present two alternate scenarios, a relatively optimistic one assuming full enforcement of current legislation (CLE), and an extremely optimistic one assuming maximum feasible reduction (MFR) of emissions based on implementation of all currently available technology without regard to cost. The CLE scenario shows a modest 13% increase in global NO_x emissions by 2030 relative to 2000. The MFR scenario shows a decline to 35% of present-day emissions by 2030. Reductions in fossil fuel use to meet climate stabilization targets would also decrease the NO_x emissions relative to the SRES projections (Smith and Wigley 2006).

Such optimism must however be tempered by observations of recent trends. Measurements of tropospheric NO_2 from space have shown a doubling of NO_x emissions from China over the 2000–2006 time period (Zhang et al. 2008a), much faster than projected by any of the SRES emission scenarios. In the United States, NO_x emissions from power plants have decreased in response to recent regulations (Frost et al. 2006), but there is some evidence from atmospheric observations that the NO_x source from motor vehicles has increased (Parrish 2006; Boersma et al. 2008), contrary to emission trends reported by EPA. Data for 1984–2004 from the National Atmospheric Deposition Program show a large increasing trend in ammonium deposition (Lehmann et al. 2007), suggesting an increase in nitrogen cycling from agriculture. Such an increase would affect soil and livestock NO_x emissions, already thought to be underestimated in current inventories (Martin et al. 2003; Bertram et al. 2005; McElroy and Wang 2005).

For methane, the CLE scenario gives results similar to SRES. However, observations over the past decade show a leveling of methane concentrations (Forster et al. 2007). It is thus possible that the SRES scenarios for methane are too pessimistic, though it is also possible that the present plateau is only a temporary reprieve (Wuebbles and Hayhoe 2002). Positive feedback of climate change on methane emission from wetlands and thawing permafrost could be a major driver for increasing methane in the future (Gedney et al. 2004)

Global SO_2 emissions are projected to increase over the next few decades (except in the B2 scenario) but then to level off and start decreasing between 2020 and 2040 reaching emissions below present levels after 2050 (Smith et al. 2005). The short-term increase in projected emissions is driven mainly by China and India, and the eventual decrease reflects implementation of coal washing, scrubbers, and a transition away from coal. More recent evidence suggests that SO_2 emissions from China may decrease sooner than indicated in the scenario as SO_2 scrubbers are now being installed on new power plants. As SO_2 emissions decrease, sulfate concentrations will decrease essentially simultaneously, hence removing the negative

Fig. 11.9 Surface temperature change in °C due to short-lived gases and particles during northern hemisphere summer for 2100–2091 *vs*. 2010–2001 in the GFDL model. (Levy et al. 2008b)



radiative forcing of sulfate from the atmosphere. Recent estimates of black carbon (BC) and organic carbon (OC) emissions for the years 2030 and 2050 also project decreases in global emissions relative to 1996 (Streets 2007). However, the magnitude of emission reductions varies greatly depending on which IPCC SRES storyline is followed (A1B, A2, B1, and B2) in the development of the projections and which region of the world is considered with emissions from South America potentially even increasing (Streets 2007). The relative rate of change of aerosol concentrations in the atmosphere will have a large impact on radiative forcing. As shown in Fig. 11.9, the combination of increasing BC and decreasing sulfate along with increases in OC and ozone is projected to result in a 1–2°C net increase in summer temperatures over most of North America in 2100 (Levy et al. 2008a, b).

Streets et al. (2009) projected future mercury emissions out to 2050 on the basis of the IPCC (2001) scenarios. They find a global change in emission relative to present ranging from −4 to +96% depending on the scenario. The trend is mainly driven by increased coal use in the developing world, principally China and India which already dominate the global mercury emission inventory (Selin 2005). The fraction of total mercury emitted in elemental form is expected to decrease from 65% today to 50–55% by 2050, which would tend to reduce global-scale transport. This decrease is due to reductions in industrial (non-coal) emissions, which have a low Hg(II)/Hg(0) ratio relative to coal combustion (Pacyna et al. 2006).

11.5 Time Scales and Implications for Accountability

The rate of change in anthropogenic emissions affecting ozone, PM, and mercury has accelerated over the past decade. This reflects on the one hand vigorous emission controls in North America and Europe to meet increasingly stringent air quality objectives, and on the other hand rapid growth of emissions in China (and to a lesser extent India) from industrialization. This shift is clearly apparent from satellite observations (Fig. 11.10). It has important implications for both climate change

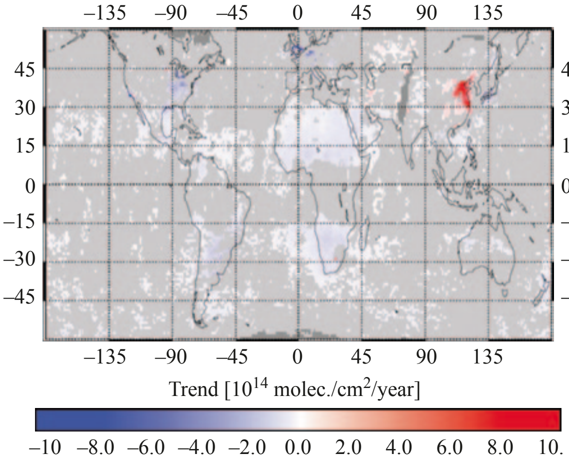


Fig. 11.10 1996–2005 trends in tropospheric NO_2 columns as observed by the GOME and SCIAMACHY satellite instruments. (van der A et al. 2008)

and intercontinental pollution. Meeting ozone and mercury air quality standards in North America in the future is likely to be increasingly on external pollution sources outside North America, making the development of international policies and agreements increasingly important.

In the case of mercury, rapid change in global emissions (Fig. 11.2) is likely to obfuscate benefits from North American emission controls, except at sites immediately downwind of major point sources where high mercury deposition is of local origin (Keeler et al. 2006). In the case of ozone, intercontinental pollution influence acts mainly to increase background ozone concentrations with peak ozone concentrations largely a result of regional emissions of ozone precursors.

Effects of climate change on air quality are expected to develop over a time scale of decades, corresponding to the time scales for climate change (Lin et al. 2007). Direct observation of these effects will be difficult because of the confounding effect from regional changes in emissions. However, it should be possible to monitor long-term trends in air pollution meteorology, in particular the frequency of stagnation episodes. Leibensperger et al. (2008) report a decrease in the frequency of mid-latitudes cyclones ventilating the northeastern United States over the 1980–2006 time period, consistent with expected trends from greenhouse warming. Combining this information with the strong observed interannual correlation between cyclone frequency and ozone pollution episodes, they conclude that the 80 ppbv standard for ozone at that time period would largely have been met in the region by now were it not for climate change.

International policies for reducing hemispheric-scale pollution can be monitored and evaluated by satellite observations of atmospheric composition, which represent a major new development in the observation system for global atmospheric chemistry over the past decade. Inverse model analyses applied to satellite observations of NO_2, formaldehyde, methane, and CO have been used to improve national and global emission estimates for NO_x (Martin et al. 2003), VOCs (Shim et al. 2005), methane (Bergamaschi et al. 2007), and CO (Stavrakou and Müller 2006). They have been used to monitor decadal trends in NO_x emissions from the United States

(Frost et al. 2006) and worldwide (van der A et al. 2008), and to detect changes in emissions on a weekly or event time scale (Beirle et al. 2003; Wang et al. 2007). Adjoint approaches to inverse modeling allow satellite data to constrain emissions at the scale of individual cities (Kopacz et al. 2009). Satellite observations of ozone and PM have also been used to test models of intercontinental transport (Heald et al. 2006; Zhang et al. 2006). As discussed in Chap. 10, the present observing system, if sustained in the future, should make it possible to monitor and diagnose the effects of changes in certain global pollutant emissions on background air quality on a decadal time scale. It would also allow for comparison of projected with actual emissions, adding an additional element of accountability.

11.6 Climate Mitigation, Air Quality Management, and Technological Change

In the long run, the most consequential effects of climate change on air quality may arise from the technological changes that will be required to minimize anthropogenic influences on the Earth's climate. Achieving the objectives of the United Nations Framework Convention on Climate Change (http://unfccc.int/resource/docs/convkp/conveng.pdf)—"stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system"—requires capping the atmospheric concentrations of long-lived greenhouse gases at some yet-to-be-determined value. Achieving this goal means that at some point in the future the net emissions of these gases must decline until a desired steady-state capping concentration is reached. The emission trajectories required depend on the capping concentration. The lower the concentration, the more rapidly emissions must be reduced. In addition, reductions in BC (a particulate with adverse health effects, a short lifetime and a high radiative forcing) would provide a rapid reduction in positive radiative forcing and could decrease the rate of global warming in the short-term (Kopp and Mauzerall 2010). How an emission trajectory may be achieved depends on many factors such as global population growth, levels of and diversity in global economic development, the goods and services demanded by these economies, the energy needed to deliver these goods and services, the current and future technologies available to supply this energy, the performance of these technologies (and how they change with time), when future technologies may become available, and the cost and availability of fuel sources.

This dependency is illustrated in Fig. 11.11 (Clarke et al. 2007), which shows emission trajectory scenarios for CO_2 generated by three integrated assessment models: the Integrated Global Systems Model (IGSM) (Sokolov et al. 2005; Paltsev et al. 2005), the Model for Evaluating the Regional and Global Effects (MERGE) of greenhouse gas reduction policies (Manne and Richels 2005), and the MiniCAM model (Brenkert et al. 2003; Kim et al. 2006). Each of the models combines, in an integrated framework, components that simulate the socioeconomic systems and physical processes that determine the effects of human activities on the physical

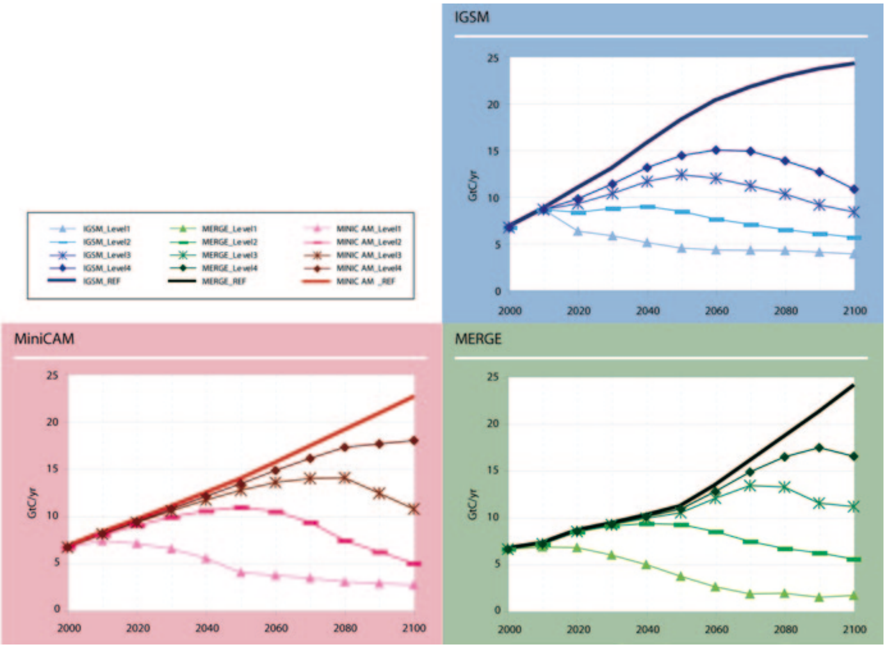


Fig. 11.11 Projected global CO_2 emissions for various GHG mitigation scenarios. Results are from three separate integrated assessment models. The *dark solid lines* depict futures in which no special actions are taken to mitigate anthropogenic climate change (i.e., business as usual). The other *curves* represent four GHG stabilization scenarios that would cap the atmospheric concentrations of CO_2 at approximately 450 ppm (*Level 1*), 550 ppm (*Level 2*), 650 ppm (*Level 3*), and 750 ppm (*Level 4*). (Results are from Clarke et al. 2007)

environment and vice versa. They differ, however, in how these systems are represented and simulated. Figure 11.11 depicts simulated global emissions of CO_2 in the twenty-first century for five different scenarios: a reference "business as usual" case (similar to the A1 scenario described in Sect. 11.2.1) and four stabilization scenarios that would cap the atmospheric concentrations of CO_2 at approximately 450 ppm (Level 1), 550 ppm (Level 2), 650 ppm (Level 3), and 750 ppm (Level 4). Each modeling group was given flexibility regarding their assumptions of population growth, economic development, and the other factors that affect future CO_2 emissions. The emission trajectories simulated by the models show significant differences, but all share common features: (1) the lower the desired capping concentration the more quickly emissions must begin to deviate from the reference scenario, (2) for capping targets of 550 ppm and above, several decades may elapse before significant reductions in global CO_2 emissions growth must occur, and (3) nearly all capping scenarios require that net CO_2 emissions reach an allowable maximum sometime within the twenty-first century.

The differences among the three models are more obvious in Fig. 11.12a, b (Clarke et al. 2007). The figure depicts how global "market share" for various en-

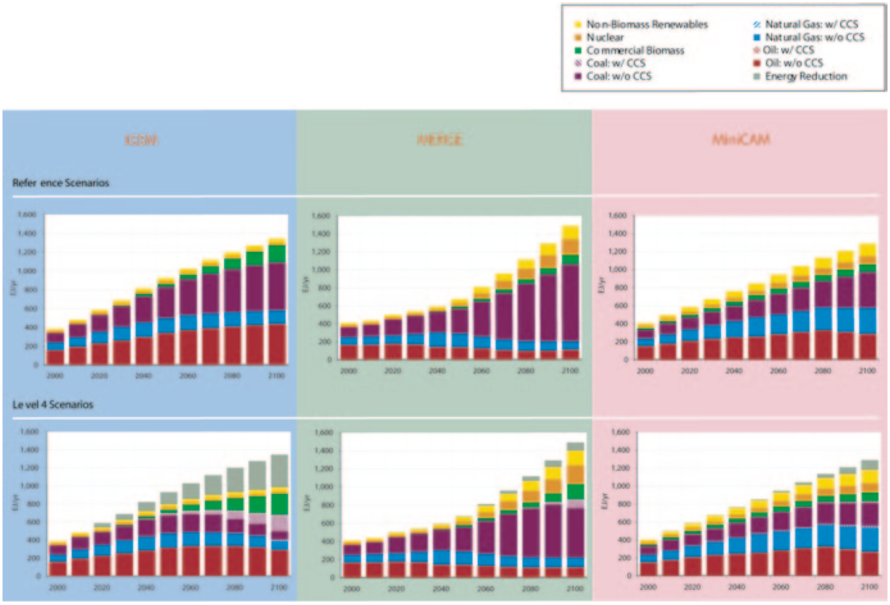


Fig. 11.12a Projected global primary energy consumption (exajoules/year) by energy source for the reference and Level 4 GHG stabilization scenarios. These scenarios are the same as described in Fig. 11.11. Energy sources considered by the models are indicated in the figure legend. Fossil fuel sources are modeled with and without Carbon Capture and Sequestration (CCS). Note that if cost effective CCS technologies are available, fossil fuels may supply significant fractions of global energy consumption even under aggressive GHG reduction scenarios (see Fig. 11.13a, b also). (Clarke et al. 2007)

ergy sources (see Fig. 11.12a for definitions) evolves in time and changes with the magnitude of the CO_2 concentration target—assuming perfect flexibility in the global deployment of energy technology or conservation measures. All of the models show that the lower the desired capping concentration, the more rapidly and fundamentally the energy supply system must change in order to meet the target. However, each model paints a significantly different picture of how this evolution might be achieved. These differences result from different assumptions about how the economy responds to environmental costs of greenhouse gas emissions, changes in the energy intensity of the global economy, the cost and availability of fuel sources and energy technologies, and the possibility of social or policy constraints on fuel sources or technologies (e.g., nuclear power). Differences among the models indicate how uncertainty about the evolution of the energy system (and the myriad emissions associated with this system) increases with time. The actual uncertainty is even greater than indicated here because we cannot know the political and socioeconomic conditions, social attitudes, or available technologies decades into the future.

The model simulations provide one important insight regarding the future: considering the cost and availability of fossil fuels (especially coal), it is difficult to envision a future energy system that does not include a major contribution from

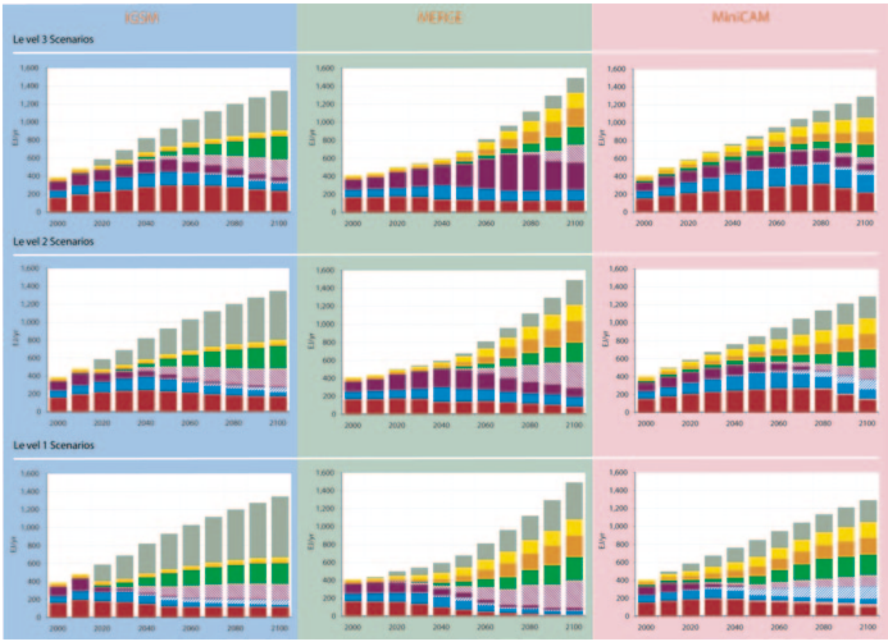


Fig. 11.12b Projected global primary energy consumption (exajoules/year) by energy source for Level 1, 2, and 3 GHG stabilization scenarios. The scenarios and suite of technologies are the same as described in Fig. 11.11 and 11.12a, respectively

fossil fuel sources, especially in rapidly developing countries. Thus, meeting the emission reduction demands of most target CO_2 concentrations implies the availability of practical and effective technologies for capturing and sequestering the CO_2 emissions from fossil fuels. Without them, meeting the most commonly discussed greenhouse gas reduction targets will be difficult. However, implementing carbon capture and sequestration (CCS) at the scale envisioned by these simulations will be a monumental technical and logistical challenge. To give an idea of the global magnitude of a future CCS industry, the three models project that stabilizing atmospheric CO_2 concentrations at about 550 ppm will require a total cumulative capture and sequestration of 140–200 Gt C by the year 2100 (Clarke et al. 2007), or approximately 20 times current annual global emissions (Fig. 11.11).

When performed at a national and energy-sector level scale, simulations such as these provide insight into how climate mitigation policies could affect future air quality. Figure 11.13a, b (Clarke et al. 2007) depicts how the energy sources for U.S. electricity production might evolve over the twenty-first century as a function of the various greenhouse gas reduction scenarios discussed previously. The figure shows that the mix of generation technologies will have to change dramatically, especially after 2050, in order to meet the more stringent greenhouse gas concentration targets. This change will clearly affect air-quality related emissions. However, these simulations also show that on a 10–20 year timescale, the mix of energy sources and

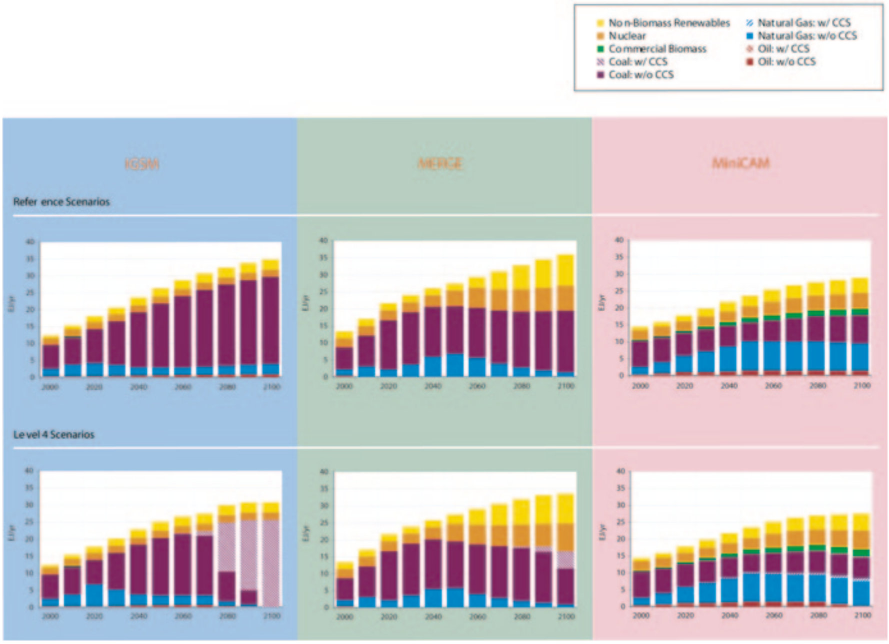


Fig. 11.13a U.S. electricity production by energy source for the reference and Level 4 GHG stabilization scenarios. The figure indicates how uncertainty concerning future fuel sources and energy technologies increases with time. Also, the lower the target GHG stabilization target (see Fig. 11.13b), the greater the projected changes in fuel-sources and energy-technologies. Figures 11.12a, b and 11.13a, b suggest that future technology and fuel-source change within a given national energy sector (here, U.S. electricity production) could be much greater than global averages. (Clarke et al. 2007)

generating technologies (and, presumably, the associated emission sources) should be fairly stable. This stability reflects the inherent inertia of the energy system. In fact, the rate of technological change may be overestimated in these simulations. In the models, changes in the energy system are driven purely by economic considerations, assuming perfect flexibility. Change in the real world could be either considerably more difficult, or significantly easier depending on political will.

The timescale issue also applies to other energy sectors. For example, for transportation, fuel sources and technologies that have been proposed for reducing greenhouse gas emissions include biofuels (e.g., ethanol and biodiesel), hydrogen, conventional and plug-in hybrids, electric vehicles, various mass transit options, and fuel cells. The air-quality related emissions from each of these options will be different. However, it will be some time before any of them can achieve significant market penetration, which provides opportunity to assess their implications for future air quality. The tools for conducting these assessments exist today. They include the air quality models described in Chap. 10 of this book and integrated assessment models such as those discussed in this section and the next. Using these tools, we can assess not only the potential effects of greenhouse gas emission reduction policies and options on air quality, but also the implications of air quality man-

Fig. 11.13b U.S. electricity production by energy source for Level 1, 2, and 3 GHG stabilization scenarios

agement decisions on climate change and climate change policy. This application is discussed further in the next section.

Researchers in Mexico have also investigated future greenhouse gas emission scenarios as part of Mexico's Third National Communication to the United Nations Framework Convention on Climate Change (INE-SEMARNAT 2006b). Greenhouse gas emissions from the Mexican energy sector were estimated for years 2008, 2012 and 2030. The estimates showed a great deal of sensitivity to GDP growth assumptions; nevertheless, the analysis indicated that near-term greenhouse gas emissions could be reduced by 17% compared to the base scenario if a number of familiar measures were adopted, such as increased utilization of renewable energy sources, implementation of stricter fuel economy standards in private gasoline-run and diesel-run vehicles, and improved energy efficiency.

11.7 Integrated Assessment Studies of the Co-benefits of Air Pollution and Greenhouse Gas Mitigation Strategies

Integrated assessment studies can be very helpful in examining mitigation strategies that could benefit both air quality and climate. Several recent integrated assessment studies have examined the co-benefits to air quality, human health and welfare, and climate change of controlling methane emissions. Fiore et al. (2002, 2008) show that reductions in methane emissions should lead to global reductions in surface ozone concentrations. The benefits of these reductions to agriculture, forestry, and non-mortality human health have been examined by West and Fiore (2005). West et al. (2006) conclude that a 20% reduction in global methane emissions, starting in 2010 and continuing through 2030 relative to a business-as-usual scenario, would result in approximately a 1 ppbv reduction in surface ozone concentrations globally with an associated reduction of approximately 370,000 premature mortalities from ozone exposure. West et al. (2007) further show that of all the ozone abatement strategies, methane emission controls appear to have the greatest benefit for mitigation of climate change (Fig. 11.14).

Ethanol is currently being promoted as a clean and renewable fuel that will reduce air pollution, climate warming and reliance on imported oil. A recent integrated environmental assessment of the production and use of ethanol as a substitute for gasoline indicates, however, that corn-based ethanol results at best in only small reductions in greenhouse gas emissions relative to gasoline (Pimentel and Patzek 2005; Farrell et al. 2006), and could cause an increase in ozone pollution due to NO_x produced as a byproduct of nitrogen fertilizer (Jacobson 2007). A recent study also finds that when the extra N_2O emission from biofuel production is calculated in "CO_2 equivalent" global warming terms and compared with the cooling effect of reducing emissions of fossil fuel derived CO_2, the result is that production of biodiesel and corn ethanol can contribute as much or more to global warming by N_2O emissions than cooling by fossil fuels savings (Crutzen et al. 2008). In addition, there are concerns that neither corn-based ethanol nor soybean-based biodiesel can replace substantial petroleum without significantly affecting food supplies. According to Hill et al. (2006), only 12% of gasoline demand and 6% of diesel de-

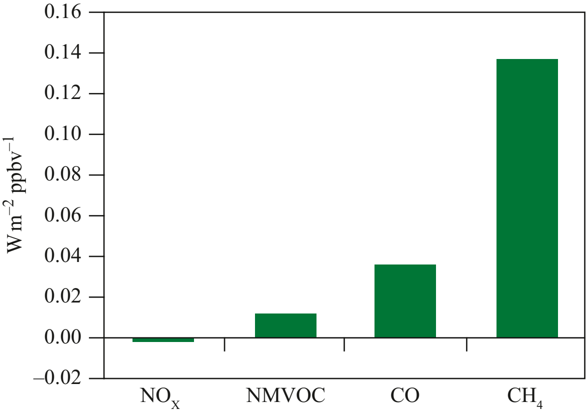


Fig. 11.14 Reductions in ozone precursor emissions have different effects on radiative forcing per unit reduction in surface ozone concentration. Shown here is the radiative forcing decrease per unit (ppbv) decrease in global surface ozone concentrations resulting from 20% global decreases in anthropogenic emissions of NO_x, non-methane VOC, CO, and methane. (Results are from global model calculations by West et al. 2007)

mand would be met if all U.S. corn and soybean production were used for biofuels. On the other hand, if ethanol were produced from non-food crops grown on agriculturally marginal land using little fertilizer, biofuel would be produced with less impact on food supplies and with greater environmental benefits (Hill et al. 2006). Use of U.S. croplands for biofuels has been found to increase greenhouse gas emissions due to resulting land-use change that brings additional land under cultivation (Searchinger et al. 2008).

Integrated assessments evaluating co-benefits of coordinated air pollution and climate mitigation efforts have been conducted for different parts of the world. The European Environment Agency (EEA) concluded that coordinated climate and air quality policy has considerable ancillary benefits including lower overall costs of controlling air pollutant emissions (EEA 2004, 2006). An examination of four megacities (Mexico City, New York City, Santiago, and Sao Paulo) indicates that greenhouse gas mitigation would lead to large reductions in ozone and particulate matter concentrations with substantial resulting improvements in public health (Cifuentes et al. 2001). McKinley et al. (2005) find that five proposed control measures in Mexico City, that were estimated to reduce annual particle exposure by 1% and maximum daily ozone by 3%, would also reduce greenhouse gas emissions by 2% (i.e., over 300,000 t of carbon equivalent per year) for both periods 2003–2010 and 2003–2020. For both time horizons, McKinley et al. (2005) estimate that about 4,400 Quality Adjusted Life Years (QALYs) would be saved.

Assessments of potential co-benefits of greenhouse gas mitigation in China have also identified large associated reductions in the emission of air pollutants. When the resulting health improvements are monetized, the emission reductions are found in many cases to be cost-effective and even profitable (Aunan et al. 2004, 2006). Conversely, a recent assessment of the effects of present and potential future emissions of BC, OC, sulfur dioxide and sulfate from China on premature mortality and radiative forcing finds that reductions in the emissions of aerosol precursors would likely reduce premature mortalities globally while increasing radiative forcing (Saikawa et al. 2009) and hence climate warming. Efforts to improve air quality in China using strategic technological choices such as advanced coal gasification technology have the potential to cost-effectively reduce air pollution and improve public health while permitting the sequestration of carbon dioxide (Wang and Mauzerall 2006). These types of focused integrated assessments examining the connection between technological options, emissions, atmospheric concentrations, impacts on health and agriculture, and associated costs have not been as common in North America. They could be very helpful in optimizing technological strategies for management of air quality and climate change.

11.8 Conclusions

Expected changes in climate and in worldwide anthropogenic emissions over the coming decades call for a global perspective in addressing future air quality problems in North America. As we enter an era of new international environmental policies directed at mitigating anthropogenic climate change, leveraging and integrating these policies with those directed at improving air quality will be highly beneficial to the achievement of both objectives.

Increasing global emissions could make it increasingly difficult to meet more stringent air quality standards in North America by means of domestic emission controls. The global distribution of pollutant emissions is changing rapidly, with decreases in North America and Europe and increases in Asia. The influence of rising Asian emissions on the problem of meeting North American air quality objectives is obvious for mercury, which is recognized to be a global pollution problem. It may become increasingly important for ozone. Models based on the IPCC future scenarios for NO_x and methane emissions project increases of 3–7 ppbv in the surface background concentration of ozone in the United States over the next two decades. Unlike mercury or ozone, rising Asian emissions are not expected to have a significant intercontinental influence on PM background in North America because of precipitation scavenging during intercontinental transport. The principal exception to this rule would be the Arctic regions of Canada and the United States.

Climate change may affect North American air quality independently of changes in pollutant emissions through perturbations to the meteorological environment, the chemical environment, and natural emissions. Simulation of regional climate is a major challenge for GCMs, and the skill of these models in describing air pollution meteorology and its trends needs to be evaluated. Nevertheless, empirical evidence exists of a relationship between increased ozone concentrations and rising air temperature. Exploratory modeling studies suggest that ozone concentrations in polluted regions of North America may increase by several ppb over the next decades as a result of climate change alone. Published modeling studies concur that ozone increases due to climate change will be largest in urban areas and where ozone is already high. In locations where ozone is relatively low, climate change may actually be beneficial due to decrease in the ozone background as a result of increasing water vapor. Unlike for ozone, there is no consensus among model studies as to the effect of climate change on PM. This reflects the complexity of meteorological effects on the different PM components. Climate-driven increases in wildfires could have a major effect. Little attention has been paid so far to the effect of climate change on mercury, but this effect could potentially be large through increased ocean volatilization and release of organic-bound mercury from soil.

Some air pollutants and their precursors can play a significant role in anthropogenic climate change and represent a potential policy lever for mitigating this problem in the coming decades. Methane, ozone, and BC combined have a positive radiative forcing (warming) as large as CO_2 according to the IPCC (2007). Sulfate, nitrate, and OC PM have a major cooling effect, both directly by scattering sunlight and indirectly by affecting cloud albedo. The cooling effect of sulfate aerosol is sufficiently large that global anthropogenic sulfate formed from the oxidation of SO_2 is thought to have greatly slowed the pace of greenhouse warming over the past century. Future reductions in SO_2 emissions to achieve air quality improvements and acid deposition reduction goals will, therefore, tend to accelerate climate warming. Reducing methane, CO, and BC emissions could offset this loss of cooling effect, while reducing NO_x emissions is thought to be climate-neutral. Reducing methane, CO, and BC emissions provide a means for short-term mitigation of climate change, but long-term mitigation will require large reductions in CO_2 emissions**.**

Projected changes in global emissions and climate could significantly complicate accountability assessments of domestic emission control policies on a decadal time scale. This is manifest for mercury, as emissions outside North America are changing rapidly and presently dominate large-scale deposition to North American ecosystems. Changes in precursor emissions on a global scale could also have an effect on ozone accountability; however, these changes would mainly affect background concentrations and would, therefore, be separable from ozone pollution episodes.

In the long run, the most consequential effects of climate change on air quality may arise from the technological changes that will be required to achieve long-term stabilization of greenhouse gas concentrations. Energy policies focused on energy conservation and use of renewable energy or other low-carbon or zero-carbon emission energy technologies such as nuclear power are likely to have major co-benefits for air quality management. However, unless multipollutant considerations are embodied in air quality management strategies, actions to improve air quality could have either positive or negative impacts on climate change. Such considerations, as well as opportunities for achieving air quality and climate co-benefits, should be assessed to ensure that air quality initiatives have no unintended consequences or result in no unintended technological or infrastructure legacy problems with regard to other environmental protection goals.

From the point of view of air quality management, the pace of technological change will generally be sufficiently slow that the air quality effects of new end-use technologies that might be adopted to address climate change can be assessed well before they achieve significant market penetration (see Chap. 8). However, the introduction of new fuels, and their related air quality and climate consequences, could take place quite rapidly if they can be supplied in sufficient quantity and readily adapted to existing technologies and infrastructure. As an example discussed elsewhere in this chapter, early assessments of the effects of increased use of biofuels (e.g., ethanol) have raised questions regarding its benefits for air quality as well as for net reduction of greenhouse gas emissions.

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Chapter 12

Past Examples of Multipopllutant Air Quality Management and Accountability

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Chapters 5 through 10 address the information needed for implementing risk- and results-based multipollutant air quality management and the tools that are available for supplying this information. These tools include: (a) emission characterization, (b) air quality modeling, (c) ambient measurements and observations, and (d) the information gained through the combined application of all three, which is often termed "weight-of-evidence". Each of these tools is an important element in the air quality management process outlined in Figs. 3.1 and 3.2. Together with knowledge of health and ecological effects, they represent the basic resources for identifying hazards and for projecting the expected outcomes of alternative management choices for improving air quality. They also provide the basic resources for determining the effect or consequences of management actions.

In this chapter, we examine representative cases in which past air quality management actions can be shown to have used elements of multipollutant air quality management and can be tested for demonstrating accountability. Accountability is the process for determining whether

- A given management action was implemented as designed and the expected emission reductions have taken place.
- The actual or estimated emission changes resulted in the expected changes in ambient concentrations or deposition.
- The changes in ambient concentrations or deposition have resulted in reductions in exposure of humans or ecosystems to the pollutants in question.
- These reductions have led to improved public health or reduced damage to sensitive ecosystems.

Historically, accountability assessment has consisted mainly of documenting changes in emissions and corresponding changes ambient concentrations for a given regulated pollutant or suite of pollutants. Much less attention has focused on determining whether these changes have resulted in verifiable (as opposed to mod-

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eled) improvements in exposure or human or ecosystem health. Perhaps the most complete exercise of accountability comes from assessment of the health benefits of reductions in primary pollutants such as lead and carbon monoxide. The accountability assessment for lead is summarized in Text Box 3.4. Even in this well-known case, the health-effects story is incomplete. Although reductions in ambient concentrations of lead were found to correlate with reduced levels of lead in blood samples, lead concentrations in blood are only an indicator of exposure. Reductions in neurotoxicity, the desired health outcome, were inferred by assuming that neurotoxicity is proportional to blood lead concentrations.

In this chapter, improvements in air quality derived from past air quality management actions are summarized briefly for criteria pollutants and some hazardous air pollutants. This summary is followed by a more in-depth analysis for five pollutants, which illustrates the kinds of accountability studies that have been performed. The in-depth examples include photochemical oxidants, airborne particles, acidic deposition and its precursors, hazardous air pollutants, and mercury. In each of these cases, "weight of evidence" using modeling projections, emissions and ambient data are used for designing reduction strategies, as noted in the first bullet above. The strengths and weaknesses of the accountability assessments are noted with respect to the four steps in the accountability chain described above. The usefulness of these assessments for providing feedback to improving the air quality management process (see Fig. 3.2) is summarized in the form of "lessons learned."

12.1 Overview of Emission Reductions and Air Quality Trends

Many investigations of air quality trends have been conducted on national scales and within state, provincial, and local domains. These are frequently provided as annual summaries and are available from air quality management authorities (e.g., see EPA 2008 for the United States or http://www.ec.gc.ca for Canada). While the magnitude and even direction of trends varies by location and country, Tables 12.1 and 12.2 provide national-scale overviews of reductions in emissions and improvements in ambient air quality for the United States and Canada. For Mexico, trends in emissions and ambient air quality have been documented mainly for Mexico City. These trends and are listed in Table 12.3.

Table 12.1 shows that since 1980, U.S. ambient air quality has improved on a national scale. However, these improvements have not been proportional to the reductions in emissions except for lead and NO_x. The declines in ambient concentrations for SO_2, CO and PM_x differ substantially from the cited reductions in emissions, and the reduction in ozone concentrations—a pollutant for which attainment has been difficult to achieve—is much less than for its precursors, NO_x and VOC. Nevertheless, these emission reductions have enabled attainment of air quality standards for CO, SO_2, NO_x, PM_{10}, and lead (pre-2008 standard) in most U.S. urban

Table 12.1 U.S. national-level changes in selected pollutant concentrations compared with emission reductions[a] for two periods of time between 1980 and 2005. Negative numbers indicate reductions or improvements. (Source: http://www.epa.gov/airtrends/2006/aq_summary_2005.html)

Percent change in emissions			Percent change in air quality		
	1980–2005	1990–2005		1980–2005	1990–2005
NO_x	−30	−25	NO_2	−37	−25
SO_2	−42	−35	SO_2	−83	−48
PM_{10}[c]	−68	−38	PM_{10}	–	−25
$PM_{2.5}$[c]	–	−13	$PM_{2.5}$	–	−7[b]
CO	−50	−38	CO	−74	−60
Pb	−96	−40	Pb	−96	−38
VOC	−47	−31	O_3 (1-h)	−28	−12
			O_3 (8-h)	−20	−8

[a] Average U.S. reductions between 1996 and 2006 reported by EPA (2008) show a VOC reduction of about 10%. Evidently, most of the VOC reductions can be attributed to the period prior to 1996

[b] Based on percentage change from 1999

[c] Includes only directly emitted particles

environments. With respect to $PM_{2.5}$, the standard for this pollutant is relatively new, and attainment remains a problem in some cities.

National trends for Canada are listed in Table 12.2. The table indicates that over the past decade or more, major reductions in the primary pollutants of concern have been achieved. As in the United States, the exception has been ozone. Ambient concentrations of this pollutant have declined overall, but not nearly as much as NO_x and VOC emissions. Furthermore, average urban ozone concentrations have increased slightly in Canada, which evidently reflects conditions in the Hamilton-Toronto region, Montreal, and Vancouver. Given the distribution of sites in Canada, the urban average is weighted toward conditions in the eastern parts of the country. There are certain inconsistencies in these results that reveal the limitations of assessing accountability through national averages, particularly in Canada, where sources outside the country can have significant impact. For example, sulfate, a major component of $PM_{2.5}$ has declined much less than $PM_{2.5}$ mass concentrations, and much less than its precursor (SO_2). These differences arise from the fact that sulfate tends to be more regionally dispersed. Thus, the sulfate component of $PM_{2.5}$ is more likely to be influenced by long-range and transboundary transport compared to components (e.g., organic and black [elemental] carbon), which are more impacted by local emissions. Further, significant SO_2 emissions in Canada come from a relatively small number of point sources, many of which are far from the urban monitoring sites. Nonetheless, the data in Table 12.2 indicate substantial improvement in the ambient concentrations of all the reported pollutants, except ozone.

The emissions and ambient pollutant concentration trends depicted in Table 12.3 reflect the major effort undertaken since 1986 in Mexico City to address pollution. The reductions in pollutant concentrations associated with primary emissions (NO_2, SO_2, TSP, PM_{10}, and CO) are dramatic, especially for SO_2. Within the expected uncertainties of the emission inventory for the city, the ambient concentrations of primary pollutants have declined in proportion to the decreases in emissions. With

Table 12.2 Selected pollutant trends from Canadian emission estimates and ambient monitoring observations between 1990 and 2006

Pollutant	National emission changes (%)	Measure	Year difference	Percent reduction
Ozone (urban sites)		Seasonal mean of daily 8 h max.	(2004–2006) −(1990–1992)	3.4[e]
Ozone (rural sites)		Seasonal mean of daily 8 h max.	(2004–2006) −(1990–1992)	−8.5[e]
NO_x (urban sites)	<−5[a]	Annual mean	(2006–1990)	−44
NO_2 (urban sites)		Annual mean	(2006–1990)	−34
VOC (urban sites)	−20[b]	Annual mean	(2006–1990)	−46
HC (non-biogenic C2–C12) (urban sites)		Mean (May–Sept.)	(2006–1991)	−62
$PM_{2.5}$	−20[c]	Annual mean	(2006–1985)	−41
$PM_{2.5}$		98th percentile	(2006–1985)	−40
Sulfate		Annual mean	(2006–1990)	−16[e]
SO_2 (urban sites)	>−30[d]	Annual mean	(2006–1990)	−54
$PM_{10\text{-}2.5}$		Annual mean	(2006–1985)	−41

[a] Partially offsetting a reduction of 25% in the transportation sector and decreases in the industrial sources are increases in the western and far eastern petroleum sectors

[b] Reductions from the transportation, industrial and solvent use sectors, were partially offset by the western petroleum sectors

[c] With open sources excluded, about 50% reduction. Reductions have occurred in industrial sectors, including wood, pulp and paper industries, and fossil fuel electricity generation

[d] Major reductions have occurred in the non-ferrous smelting and refining sector, fossil fuel electricity generation with smaller reductions from the industrial and transportation sectors. These have been partially offset by increases in the western and eastern petroleum sectors

[e] The 2008 Canada-U.S. Air Quality Agreement (International Joint Commission) Progress Report shows decreases in emissions, acidic deposition and ozone along the border region of the two countries. (http://www.ijc.org[accessed March 2009])

Table 12.3 Approximate percentage changes in annual emissions and average ambient concentrations for selected pollutants in Mexico City—1990–2006, 2008. (Source: Secretaría del Medio Ambiente del Gobierno del Distrito Federal, Sistema de Monitoreo Atmosférico)

Emission[a]	Percent change	Air quality	Percent change
NO_x	−26	NO_2	−34
SO_2	−91	SO_2	−88
Particulate matter	−50	TSP	−64
		PM_{10}	−57
CO	−62	CO	−75
VOC	−41	VOC	–
Ozone	NA	Ozone 1-h max	−38
		Ozone 8-h max	−36

[a] 2006 MCMA Emssions Inventory

respect to ozone, decreases in ambient concentrations are larger than the changes reported in the cities of Canada (e.g., Fig. 12.2) and the United States. Outside Mexico City changes in ambient air quality generally have not been measured. Thus, nationally aggregated trends are not available.

These summaries indicate that air quality management practices have achieved major reductions in the ambient concentrations of major air pollutants. However as the summary tables suggest, the effectiveness of these practices has varied. Important challenges remain for reconciling reported reductions in emissions with measured changes in ambient concentrations, especially for pollutants formed by secondary reactions in the atmosphere such as ozone and the secondary component of particulate matter. Reconciling emission changes with trends in ambient concentrations involves the first two steps in the accountability process. The next steps entail determining whether exposure, health, and ecosystem effects have been mitigated. Completing these steps is far more difficult, even considering the long history of research on the effects of air pollution. The remainder of this chapter discusses these issues in more detail using five examples.

12.2 Examples of Multipollutant Trends

12.2.1 Complexities of Ozone Reduction

Summary Reductions in ozone concentrations depend on reductions in its precursor emissions, NO_x and VOC. Because ambient ozone concentrations are a complicated function of precursor concentrations and meteorological variability, projecting changes involves application of complex models in combination with evaluation of ambient concentration changes. Emissions of ozone precursors have declined since the 1970s, as verified by declines in ambient concentration measurements. The effects of precursor changes are observed in the decline in maximum ozone concentrations in most urban areas of North America. However, the expected ozone concentration reduction from design strategies generally has not been verified retrospectively with actual observations. Translation of ambient ozone concentration maxima to human or ecosystem exposure and effects, and consequent changes therein have not been documented quantitatively. Human health effects from outdoor exposure to ozone have been studied extensively, but *improvements* in human health status with ozone reductions remains to be demonstrated, despite tracking of ozone concentrations for more than three decades.

In 1970, photochemical oxidants were designated a criteria pollutant (CP) in the United States with a focus on one particular oxidant—ozone[1]. Later, ozone alone was identified as the CP. Canada and Mexico also identified ozone as a regulated

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[1] In addition to ozone, photochemical oxidants include short-lived oxygenated intermediates, peroxides, nitric acid, and NO_3 radical. These species are estimated to represent about 10% of the total oxidant concentration; the remainder is said to be ozone.

pollutant and adopted ambient concentration standards for it. In Canada, air quality management attention was initially focused on the Hamilton-Toronto, Ontario area. Subsequently, Vancouver, British Columbia was added as an urban area of concern. In Mexico, Mexico City has received the greatest attention, but in recent years air pollution in urban communities along the U.S.-Mexico border and elsewhere has begun to be addressed.

In the United States, EPA initially chose to reduce ozone using a VOC-only reduction strategy (e.g., EPA 1971). With additional knowledge, a combined VOC and NO_x precursor reduction strategy was found to be necessary to achieve further reductions in ambient ozone (e.g., NRC 1991; NARSTO 2000). This overall strategy of attacking the ozone problem by targeted reductions in VOC and/or NO_x emissions has remained in place throughout North America even as the standards and metrics (e.g., 1-h versus 8-h daily maximum concentrations) have changed.

Starting in the 1970s, the strategies for reducing precursor emissions focused on on-road motor vehicles and to a lesser extent on emissions from the industrial and electricity generation sectors. At first, reducing vehicle traffic in highly impacted areas such as Los Angeles was considered an emission reduction tool, but this idea was soon abandoned as impractical. Instead, large investments were made in technologies for reducing VOC and NO_x emissions in light-duty vehicles. These investments resulted in the addition of three-way catalyst units to vehicle exhaust systems in the 1980s, improvements in combustion efficiency beginning in the 1990s, and the control of evaporative VOC emissions (e.g., Sawyer et al. 2000; also Chap. 8).

More recently, heavy-duty (truck) and nonroad (construction equipment, locomotives, etc.) vehicle emissions have received increased scrutiny as reducing ozone concentrations proved to be an extremely recalcitrant problem. As vehicle emissions were targeted, petroleum, chemical and other industrial sectors were also required to reduce VOC and NO_x emissions. The electric utilities reduced NO_x emissions through combustion controls and, more recently, through selective catalytic reduction of effluents.

Location-specific VOC–NO_x emission control strategies have proven generally effective in reducing ozone concentration peaks. However, ozone levels throughout North America remain above the longer time-averaged standards in some large cities, and areas surrounding them. This persistent problem has required increasingly stringent reductions in precursor emissions from both the transportation and the stationary source sectors, as well as changes in fuel composition. Emission surveillance programs beginning with original-equipment manufacturers' engine certification requirements, inspection and maintenance programs (including periodic dynamometer testing), and periodic on-road observations of emissions from in-use vehicles, have shown a reduction in emissions from vehicles, with violations in emission levels dominated by a small fraction of vehicles in use (e.g., Sawyer et al. 2000; Vega et al. 2000; Schifter et al. 2008). Stationary-source emissions must be permitted, and some sources are audited periodically according EPA and state or local procedures. Electricity generating units now are required to reduce SO_2 and NO_x emissions (Molburg 1993), and monitor SO_2 and NO_x emissions by continuous emission monitoring systems (CEMS). As was the case for lead, emission controls for VOC and NO_x are projected to have multipollutant benefits by reducing emissions of nitric acid, organonitrates, and fuel-related or combustion-related related air toxics such as benzene, butadiene, and aldehydes (see also Sect. 12.4).

The highly non-linear relationship between ozone precursors and maximum ozone concentrations is well known to decision-makers and complicates assessment of the effectiveness of emission control strategies in reducing this pollutant. As discussed in Chap. 7, there are regimes of VOC–NO_x concentrations where change in one or the other precursor (NO_x or VOC) can lead to a reduction, virtually no change, or an increase in ozone concentration (e.g., NARSTO 2000; Reynolds et al. 2003; Geddes et al. 2009). This characteristic of ozone chemistry is important for the control of ozone concentrations in North American cities. It also underlies the difficulty in relating aggregated changes in ozone concentrations to reductions in VOC or NO_x emissions, as illustrated in Tables 12.1, 12.2, and 12.3. Tracking long-term changes in ozone concentrations as a function of its precursors was further complicated by a regulatory action in 1996, which changed the U.S. NAAQS from a 1-h maximum to a daily maximum based on an determination of the 4th highest 8-h mean concentration over three year intervals. This change expanded the time period over which nonlinear chemical processes, as well as meteorological variations that also affect ozone concentrations (e.g., Reynolds et al. 2003) can occur.

Both the assessment and design of ozone and related oxidant management actions can be further complicated by variations in the chemical reactivity of VOC emissions (Lueken and Mebust 2008; Hales et al. 2007). Differences in reactivity are generally not accounted for in ozone reduction management, but they could be considered to improve the efficiency of VOC emission reductions.[2] Another complicating factor is natural emissions. In the eastern United States, especially the Southeast, ozone production is also partly a function of natural hydrocarbons, especially isoprene (e.g., Chameides et al. 1988; NARSTO 2000). As reductions in anthropogenic VOC emissions continue, the role of natural VOC emissions becomes more important in many locations (e.g., Reynolds et al. 2003; Geddes et al. 2009).

Investigations of regional ozone chemistry and transport for the eastern United States and southeastern Canada indicate that ozone formation takes place on an urban scale and in accumulated polluted air over a larger region (Wolff and Lioy 1980; NARSTO 2000). This result was also found to apply along the Mexico-U.S. border, especially between California and Mexico and Texas and Mexico. These discoveries have affected interstate and trans-national ozone management strategies, and they were examined by the Ozone Transport Commission, the Ozone Transport Assessment Group, and the International Joint Commission in the 1990s. As part of these examinations, extensive regional-scale air quality modeling was performed to seek options for multi-state emission controls. The results of the Ozone Trans-

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[2] Selective VOC reduction by reactivity is under consideration as an efficient means of managing ozone, and one formal U.S. action has been taken for consideration of organic coatings. In some states, e.g., California, VOC reactivity is taken into account in the management of VOCs to reduce ozone concentrations (e.g., Avery 2006).

port Assessment Group computations suggested that NO_x emission reductions were favored regionally, while both NO_x and VOC reductions were required for local urban management. This finding supported EPA's NO_x state implementation plan requirement (NO_x SIP Call) in 1997 for widespread electric utility NO_x emission reductions across the eastern United States. These developments also reinforced interest in regional scale, multistate, and Canadian-U.S. transboundary planning for air quality management similar to what had been considered earlier for acid deposition reduction (e.g., http://www.ijc.org).

12.2.2 Oxidant Air Quality Trends and Emission Reductions

The results of evolving policies for reducing ambient ozone concentrations across the United States have been tracked and compared with changes in precursor emissions, principally NO_x (e.g., Bachmann 2007). These analyses have shown that reductions in ozone have occurred despite large increases in the number of vehicles on the road and in vehicle miles traveled. Mexico City has experienced similar reductions in the 1990s after major efforts were taken to reduce transportation emissions (see Table 12.3). Trends in U.S. ozone concentrations by region are shown in Fig. 12.1. Although the effectiveness of ozone reduction strategies varies by geographical region, the tendency is to approach or achieve the 1996 U.S. ambient standard of 80 ppbv 8-h ozone maximum.[3]

Assessment of declines in ozone concentration as an indicator for air quality improvement also can reflect changes in other oxidant species. One such example is the trends in the organonitrate oxidation products, peroxyacetylnitrate (PAN) and peroxypropionylnitrate (PPN). Grosjean (2003) analyzed long-term data for these chemicals and showed that their concentrations in Los Angeles air steadily declined between 1960 and 1997, qualitatively in parallel with reductions in the oxidant indicator, ozone.

Wolff et al. (2001) reported a summary of U.S. ambient VOC and NO_x concentration data for 1985–1996, which confirmed a decrease in both of these precursor concentrations that correlated with reductions in 1-h maximum ozone concentrations. Wolff et al.'s (2001) investigation of Canadian ambient data from 1985 to 1993 suggested no significant trends in ozone precursors during this period, but more recent Canadian analyses of ambient data suggest both VOC and NO_x reductions have occurred (Table 12.2).

Changes in ozone precursor emissions also have been achieved by improvements in engine combustion management, improved vehicle maintenance, and by changing the composition of gasoline to reduce more reactive species in favor of other components. For example, Bishop and Stedman's (2008) studies assert that

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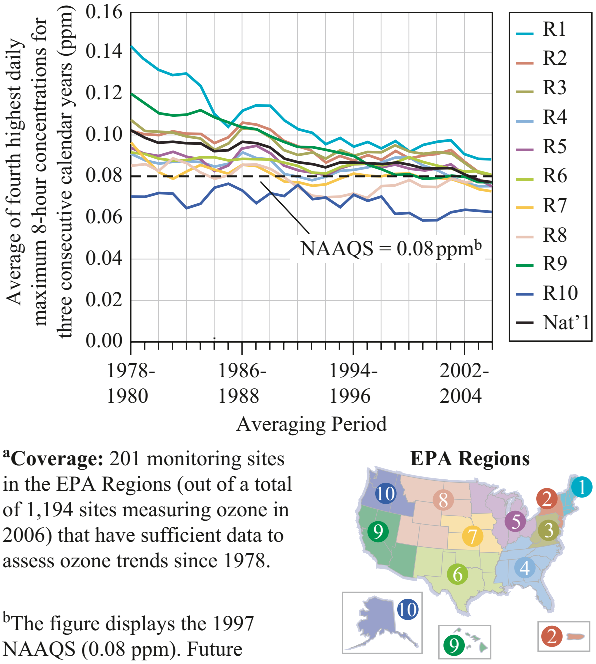
[3] As of March 2008, the U.S. NAAQS was changed by the EPA Administrator from 0.080 ppm 8-h average of daily maxima to 0.075 ppm 8-h average of daily maxima, changing the non-attainment designations across the country.

Fig. 12.1 U.S. trends in the 8-h maximum daily ozone concentrations (prior to the 2007 air quality standard) by geographic region. (Source: EPA 2008)

Ambient 8-hour ozone concentrations in the contiguous U.S. by EPA Region, 1978-2006[a]



[a]**Coverage:** 201 monitoring sites in the EPA Regions (out of a total of 1,194 sites measuring ozone in 2006) that have sufficient data to assess ozone trends since 1978.

[b]The figure displays the 1997 NAAQS (0.08 ppm). Future versions of the Report on Environment (ROE) will compare ozone concentrations to the recently promulgated 2008 NAAQS (0.075 ppm) or to the NAAQS in effect at the time.

the steady reduction in light duty vehicle NO_x and VOC emissions in the United States have come primarily from improvements in engine combustion monitoring and inspection/maintenance programs. Gasoline blend changes probably had minor effects on these reductions. On the local scale, these changes may be offset by differences in vehicle fleet conditions, industry, and growth in traffic.

Urban trends for ozone concentrations are of considerable interest for providing insight into the effectiveness of reduction strategies for precursor emission on these scales. This is particularly true for cities where photochemical activity is known to be high. Examples of such cases, with respect to each country, are Los Angeles, Mexico City, and southern Ontario, which is partially influenced by the Hamilton-Toronto metropolitan area. These examples illustrate the changes in ozone concentrations that have occurred over a number of years, despite a steady increase in population, a steady increase in vehicle usage, and changing industrialization. Trends in ozone concentrations in these metropolitan areas are shown in Fig. 12.2. The Los Angeles and Mexico City metropolitan areas are megacities of population

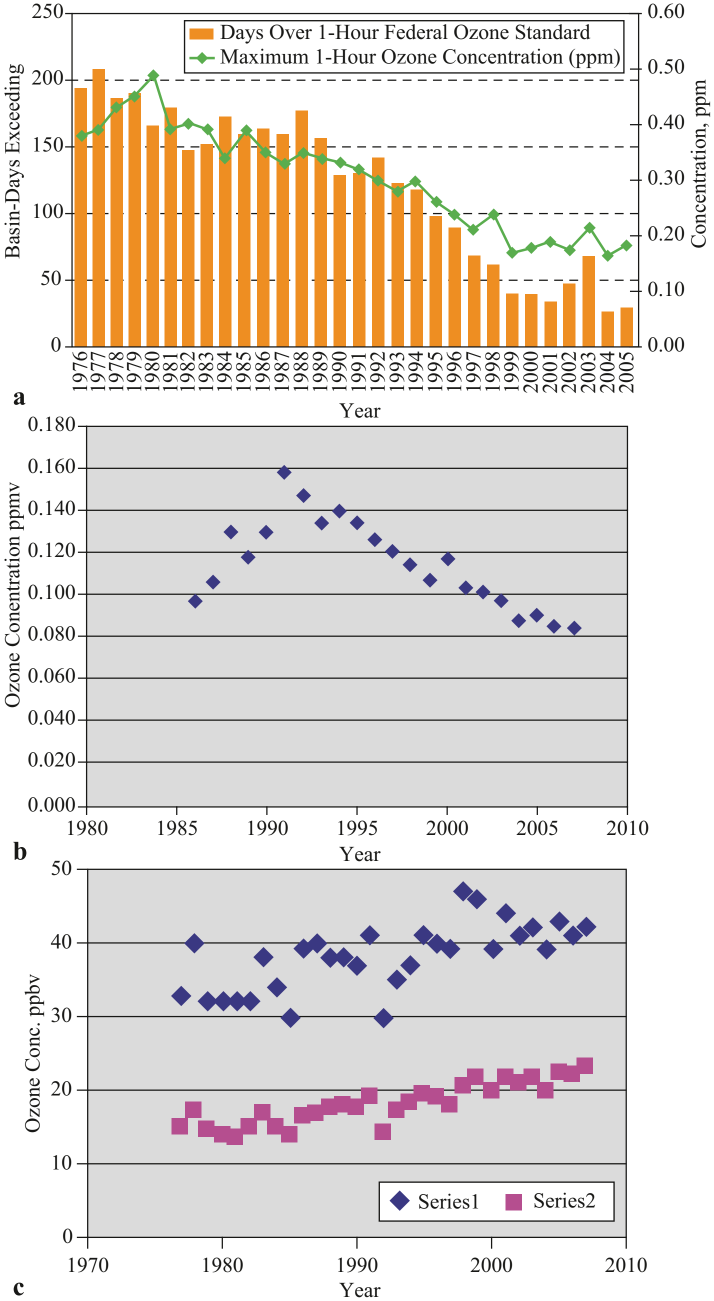


Fig. 12.2 Examples of trends in ozone concentration in three metropolitan areas. **a** Los Angeles metropolitan area number of days exceeding the NAAQS and maximum 1-h ozone concentrations (SCAQMD 2007). **b** Mexico City and the Valley of Mexico (based on average of 1-h daily maxima—Secretaria del Medio Ambiente del Gobierno del Distrito Federal, Sistema de Monitoreo Atmos.). **c** East Toronto site (Series 1 = 90th percentile of hourly average concentrations; Series 2 is the mean of the hourly average concentrations). (Source: Ontario Ministry of Environment 2006)

larger than 10 million, which are relatively isolated from the impacts of regional pollution transport. Southern Ontario, on the other hand, is affected both by a long-range transport component and by its own local photochemistry.

The trends for Los Angeles and Mexico City are spatial averaged maxima computed from monitoring sites in the two metropolitan areas. The trends for Toronto are based on an eastside suburban site, and indicate the 90th percentile values for the years sampled. In contrast to Los Angeles and Mexico City, the Toronto site depicts increasing maximum ozone concentrations. However, the trends for the Province of Ontario (not shown in the figure), including rural areas and smaller cities, generally show a declining average 1-h maximum from 1980 to 2007. A possible explanation for the positive trend measured at the East Toronto site is that large local decreases in ambient NO concentrations have led to reduced levels of destruction (i.e., titration) of ozone entering the city from regional or long-range transport (e.g., OME 2006).

Recently, Geddes et al. (2009) investigated trends in ozone for the Toronto area in more detail. They concluded from examination of trends in VOC reactivity and NO_x ambient data and air quality modeling experiments that precursor conditions in the city were consistent with an expectation of little change in 8-h maximum ozone concentrations—a conclusion which supports the observations. The modeling experiments indicate that the reasons for observed increases in maximum ozone concentrations in Toronto are more complex than just a decline in NO titration of ozone. The reasons may be more related to the NO_x/VOC regime that has existed in the city since the early 2000s (Geddes et al. 2009). They also reported that ozone concentrations in Toronto are quite sensitive to the maximum air temperature during the day. Analysis of ozone concentrations by wind sector indicated that Toronto experiences high baseline concentrations of ozone when there is air mass transport from the south. This transport adds to the ozone that is generated locally. Overall, the Geddes et al. (2009) analysis reinforces the conclusion that the complexities of ozone chemistry, meteorology, and long-range transport make it difficult to evaluate the effectiveness of ozone control measures. This is a conclusion that was becoming evident in southern California as early as the 1950s (e.g., Neiburger and Edinger 1954) and thus continues to present challenges to this day.

While analysis of the data supports the conclusion that NO_x and VOC precursor reduction strategies are generally successful in reducing ozone concentrations, examples like Toronto continue to exist where these strategies seem to have been less successful. Moreover, even where these strategies have reduced ozone concentrations, these reductions do not prove that the precursor emission reductions were truly optimal. Furthermore, it is usually not known whether the ozone reductions resulting from an air quality management action are consistent with the reductions originally projected for that action (e.g., Camalier et al. 2007; Chap. 10).

Adjusting U.S. national trends in ozone concentrations for meteorological variability produces modest differences from the unadjusted trends depicted in Fig. 12.2. Porter et al. (2001) have examined the effects of meteorological variability on ozone trends. Porter et al. (2001) and others have noted that meteorological variability—diurnal, seasonal and annual—makes it difficult to detect concentra-

Table 12.4 Meteorologically adjusted ozone trends May–Sept., 1997–2006 for seven regions of North America, based on 8-h averages of ozone concentrations measured at representative sites found in each of the regions. (Sites are PC1 = Quebec (18 sites); PC2 = Northeastern United States (18 sites); PC3 = Southeastern United States (18 sites); PC4 = Southern Ontario/Great Lakes/Upper Ohio River Valley (10 sites); PC5 = Saskatchewan/Alberta (6 sites); PC7 = Canadian Atlantic (6 sites); PC9 = Canadian Pacific (4 sites). Adjustments made using a generalized linear mixed model trend analysis. (From Chan 2009; EC 2008b)

PC	Averaging period	Mean	Percent change
1	2003–2006 (T1)	35.2	−3.2
	1997–2000 (T2)	36.4	
	Diff (T1−T2)	−1.2	
2	2003–2006 (T1)	42.3	−7.9
	1997–2000 (T2)	46.0	
	Diff (T1−T2)	−3.6	
3	2003–2006 (T1)	45.2	−8.6
	1997–2000 (T2)	49.4	
	Diff (T1−T2)	−4.3	
4	2003–2006 (T1)	39.5	−4.1
	1997–2000 (T2)	41.2	
	Diff (T1−T2)	−1.7	
5	2003–2006 (T1)	38.5	0.0
	1997–2000 (T2)	38.5	
	Diff (T1−T2)	0.0	
7	2003–2006 (T1)	36.5	2.1
	1997–2000 (T2)	35.7	
	Diff (T1−T2)	0.8	
9	2003–2006 (T1)	31.8	5.2
	1997–2000 (T2)	30.2	
	Diff (T1−T2)	1.6	

tion trends resulting from changes in emissions. Trend estimates can differ, even for the same location, depending on the methods adopted for reducing non-trend variation in the concentration time-series. Accounting for these effects requires long-term records of both air quality and meteorology.

Chan (2009) recently carried out a rigorous analysis of North American ozone concentration trends by comparing two different three year averaging periods. The results are summarized in Table 12.4 (Chan 2009; EC 2008b). To account for meteorological variability, Chan included the effects of temperature, relative humidity, wind speed, air mass trajectory clusters, and precipitation in a generalized linear model. To generate robust results, common sites were grouped into geographical regions using principal component analysis, and the meteorologically adjusted trends were then examined by region. Chan's results show a statistically significant decline in average 8-h daily maximum ozone concentrations in the four regions in the eastern half of the study area, except for the Canadian Atlantic coastal provinces where there was a 2.1% increase. Even larger increases were observed for the sites in the Canadian Pacific area. In this region, ozone concentrations increased by 5.2% between 1997–2000 and 2003–2006.

The ozone trend at one particular Canadian site is of interest because of its elevated location. This site is Round Top Ridge, which is in a rural location close to a mountain summit on the Quebec-Vermont border. This site is downwind of the industrial Midwest and southern Ontario. At times, it is also downwind of the U.S. East Coast. The elevation of the site reduces the influence of local surface emissions sources; thus it is thought to be representative of lower tropospheric ozone concentrations in this region.

Trends at the Round Top Ridge site were analyzed as a function of air-mass transport direction (EC 2008b). For 1988–2006, the overall trend at Round Top Ridge was $-0.58 \pm 0.26\%$ per year. However for air masses arriving from the northwest, meteorologically adjusted ozone concentrations declined in all seasons by $0.65 \pm 0.8\%$ per year. More importantly, for air masses originating from high-precursor emission areas of the eastern United States, significant ($\alpha = 0.5$) negative trends were observed for the summer months (when photochemical production of ozone peaks) that were two times the negative trend associated with northwesterly flow. These air masses originated over areas where there have been important emissions reductions in recent years. Also, the decreases were observed to be particularly sharp for 2002–2006, which coincides with the U.S. NO_x SIP Call. These large and significant summertime decreases are particularly interesting because summer was the initial target season for the NO_x reductions envisioned by this policy.

A complementary example of adjusting observed trends for meteorological factors is given by Zheng et al. (2007), who analyzed regional ozone trends in the eastern United States in order to assess the effects of reduced NO_x emissions from U.S. power plants due to the 1997 NO_x SIP Call. After adjusting for meteorological variability, Zheng et al. found a negative trend in ozone concentrations that they attributed to the reported reductions in NO_x emissions for the region.

Analysis of ozone trends has typically excluded consideration of possible changes in background ozone. The current hemispheric background level in North America is 20–40 ppbv or roughly one-fifth to one-half the level of the 8-h U.S. standard. There is some evidence that the background concentration in the northern hemisphere has increased in recent years,[4] probably from continental-scale pollution combined with long-range transport of pollution around the globe (see also Chap. 11).

12.2.3 Inferring Precursor Emission and Ozone Linkages

Linking changes in ozone concentrations to changes in precursor emissions through modeling or direct comparison with ambient concentrations of precursors is an important objective for accountability. From a U.S. national perspective, the com-

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[4] The current picture of increases in tropospheric ozone concentrations in the northern hemisphere is more complex that a simple monotonic increase, and varies by geographical region as noted by Oltmans et al. (2006); Vingarzan and Taylor (2003).

parison shown in Table 12.1 is instructive. The table indicates that the observed reductions in 1-h average ozone concentration for 1980–2005 and 1990–2005 were −28% and −12% respectively. Reductions in the 8-h average ozone concentrations over the same time periods were more modest, −20% and −8%. These reductions corresponded to reductions in estimated emissions of VOC and NO_x for the two time periods of −47% and −31% (for VOC) and −30% and −25% (for NO_x). The results suggest that average NO_2 concentrations responded approximately linearly to reductions in NO_x emissions. Using data in Table 12.1, the response of ozone concentrations to VOC emission controls between 1980 and 1990 was approximately linear—a 16% 1-h maximum ozone concentration reduction in response to a 16% reduction in VOC and 5% reduction in NO_x emissions. Arguably, this reflects a broadly applicable VOC limiting condition for urban atmospheres during this time period (see Chap. 7); the apparent linear response to VOC control is consistent with theory (and perhaps vindicates the 1971 U.S. focus on VOC reductions to reduce ozone levels). This linearity contrasts with the observed behavior of ozone in response to reductions in precursor emissions for the period 1990–2005. For this period, the reduction in 1-h maximum ozone concentration was 12% compared to a 31% reduction in VOC and a 25% reduction in NO_x. This result is more difficult to interpret, but possibly relates to shifting of the chemistry environment to a regime less responsive to precursor reductions (See also NARSTO 2000). Analogous arguments could be made for ozone -precursor relationships in the Canadian and Mexico City cases.

Illustrative Local Urban Cases. Studies of the effectiveness of local ozone control strategies have been conducted in several locations, especially in southern California. An example is the study by Lee et al. (2003) for the Los Angeles area (Fig. 12.3[5]). Their analysis focused on a set of ambient measurements on a ridgeline of the San Bernadino Mountains, which is in a downwind direction north and east of downtown Los Angeles. This location is known for very high levels of ozone. In the figure, daily changes in the local emissions of precursors are compared with the frequency that ozone concentration exceeds 95 ppb. Beginning in the 1980s, the figure shows a steady decline in SUM06 ozone concentration and in daily 1-h peak ozone concentration that tracks a decline in local precursor emissions and an approximately constant value for the VOC (ROG)/NO_x emission ratio. This decline in ozone concentration is observed in spite of a slight increase in daily maximum temperature—an environmental factor that generally correlates with increasing ozone. This result provides a qualitative indicator that emission reductions in the Los Angeles area have led to decreasing ozone concentrations. Results such as these give the decision maker some confidence that emission reductions have been successful in improving ozone-related air quality, but the usefulness of this kind of information for guiding future control strategies is limited.

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[5] SUM06 ozone concentration is defined as the hourly ozone concentration above 0.06 ppm, summed over 12 h (8 a.m.–8 p.m.) during a three-month period. SUM06 was intended to measure the exposure of vegetation and crops during the growing season, proposed as a U.S. secondary ambient standard.

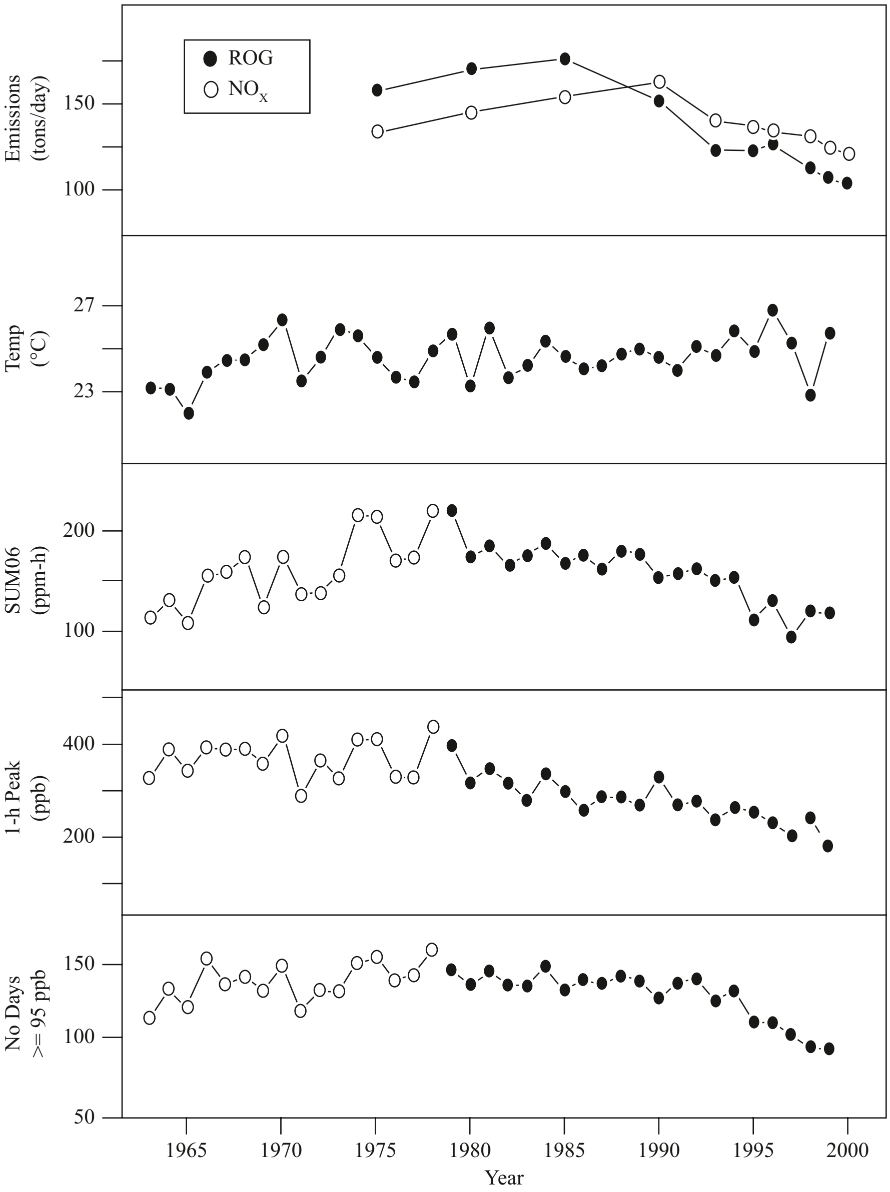

Fig. 12.3 Trends in May–September SUM06 12-h ozone concentration, peak 1-h ozone concentration and daily (California standard NAAQS) exceedances of 95 ppb at Crestline, CA (1963–1999) relative to trends in mean daily maximum temperature and daily reactive gases (ROG) and NO_x emissions for San Bernadino County. (From Lee et al. 2003)

For development of new management strategies, modeling the response of ozone to hypothetical emission changes is the prescribed method of choice. Modeling approaches include source-based computations using deterministic air quality models that incorporate emissions and meteorological inputs (e.g., Chap. 9; also Russell and Dennis 2000) and several different observationally based approaches (e.g., Hidy 2000). The latter approaches have been useful in characterizing the sensitivity of ozone formation to interactions among precursors, but these post hoc studies have been less useful in projecting the response of ozone to future emission changes.

Source-based models have improved since their inception in the 1970s as meteorological modeling, knowledge of key physico-chemical processes, and emissions have improved. Current air quality models are highly complex. They are inherently multipollutant in character, as they include within their algorithms speciated VOCs and complex photochemistry. Simulations by these models are regularly compared to observational data as a means for establishing model reliability in terms of model-measurement bias and reproducibility. Perhaps the most extensive of these intercomparisons has been done for the California urban and regional environment (e.g., Blanchard et al. 1999; Reynolds et al. 2003) and most recently for the southern Great Lakes region (Makar et al. 2010).

Although source-based modeling has been the principal tool for developing emissions reduction strategies, the projections of these models have rarely (if ever) been compared retrospectively with subsequent observed changes in ambient ozone or precursor concentrations. Reliability criteria for making such comparisons have been proposed by Roth et al. (2005), for example. Although there are many cases where emission reductions indicated by the models have failed to achieve projected urban air quality management goals, there have been few retrospective analyses of why these reductions failed, particularly for cases prior to the 1990s.

An example of retrospective analysis using ozone modeling comes from recent studies in Mexico City. Analyzing the ozone trends in Fig. 12.2b, combined with the trends in CO, VOC and NO_x emissions, Zavala et al. (2009) determined that the reduction in hourly maximum ozone concentrations in the city resulted from changes in gasoline-powered vehicle emissions. These changes have modified the atmospheric chemistry of Mexico City, shifting it from low VOC sensitivity to high VOC sensitivity. Modeling ozone production in the city using the CAMx algorithm reproduces the historical trends and the current photochemical levels. Regarding the future, the model indicates that ozone concentrations will increase linearly with NO_x emission reductions, but decrease with VOC emissions within 30% of a base case. Future VOC emission reductions will thus focus on diesel vehicles and area sources, particularly emitters of alkene, aromatic, and aldehyde compounds.

Regional Ozone. With the availability of today's improved high-speed computational tools and broadened collections of ambient data, an increased number of local and regional-scale retrospective analyses have been reported. One example is the regional-scale analysis of the post-1997 U.S. NO_x SIP Call, which provides a weight-of-evidence conclusion that NO_x emission reductions in the eastern United States have resulted in a corresponding decline in regional ozone concentrations (e.g., EPA (2007a). Kim et al. (2006) have shown through analysis of satellite data that NO_x reductions in the East have declined as would be anticipated from emission measurements. After 1997, Frost et al. (2006) evaluated NO_x emission changes for more than 50 power plants in the eastern United States, and verified CEMS-measured NO_x emission reductions using aircraft observations. The study compared ozone reductions from air quality modeling using actual NO_x emissions reductions to observed ozone. The results indicate that the observed changes in ozone concentrations reductions were consistent with expectations in areas around the power plants, and were influenced by meteorological factors, as well as by local ambient concentrations of NO_x and VOC. Analyses by Godowitch et al. (2008) and Gego et al. (2008) used regional-scale modeling to illustrate, at least qualitatively, that observed regional-scale changes in ozone concentrations in the eastern United States again were consistent with expectations from the NO_x emission reductions, as determined by the continuous emission monitoring of power plant emissions.

EPA (2007a) assessed trends in both regional and urban-scale ozone concentrations for areas surrounded by power plants whose emissions are governed by the NO_x SIP Call. Figure 12.4 shows the declines in summer maximum 8-h ozone concentrations based on both urban and rural monitoring sites. The figure shows a general decline in ozone concentrations, which is attributed to the reductions in NO_x.

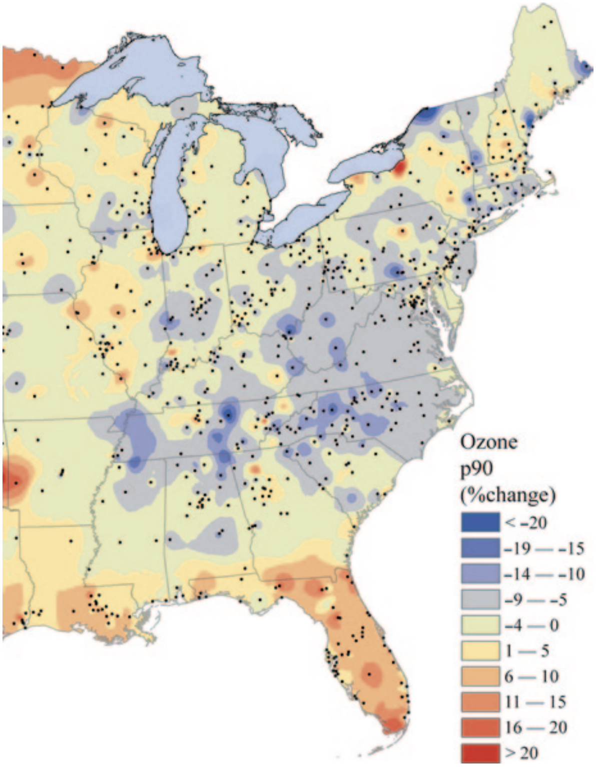

Fig. 12.4 Map of 90th percentile 1-h ozone concentration changes in average concentrations between 2000–2002 and 2004–2006. The urban and rural ozone sites used for the map are shown as *black dots*. (Source: EPA (2007a)

The EPA report does not, however, discuss the simultaneous effects of probable reductions in transportation-related NO_x and VOC emissions or the effects of natural VOC emissions on the inferred association between ozone and the power-plant NO_x reductions. By failing to consider these factors, the demonstration of accountability in this case must be considered incomplete, even for the link between power-plant precursor emissions and ambient ozone concentrations.

With the improvements in modeling and the ability to undertake daily forecasting of ozone air quality, new opportunities now exist for testing air quality model output with emission models and meteorological forecasting.[6]

12.2.4 Health and Ecological Effects of Ozone Exposure

12.2.4.1 Health Studies

Extensive study of human health effects from exposure to ozone and some related photochemical oxidants has been undertaken since the 1950s. Studies have included exposure characterization, toxicological studies, controlled human exposure studies and epidemiological investigations. Epidemiological studies have documented acute and chronic responses to outdoor ozone exposure ranging from1-h average concentrations of 600 ppbv, which were extremes observed in southern California during the 1960s, to current 1-h maxima, which can be as low as 100 ppbv. These studies, summarized by EPA (2006), have documented a range of adverse effects, from lung inflammation and dermal tissue irritation to systemic stress on the cardiovascular system.

It is widely known that exposure to air pollution outdoors is an incomplete picture of total daily exposure, since people in North America, especially in Canada and the United States, spend most of their time indoors. Total exposure to ozone depends upon how readily this gas infiltrates buildings or other enclosures such as vehicles, and the activity patterns of people in different socioeconomic classes and climatic regimes. Ozone is destroyed when it comes into contact with most surfaces, so that ozone concentrations indoors will be substantially less than outdoors (e.g., Chap. 5; also Cano-Ruiz et al. 1993; Morrison and Nazaroff 2002). Nevertheless, conventional air quality management practice relies on outdoor concentration metrics as a surrogate for exposure. While this assumption is challenged from time-to-time, it remains the keystone for the development of control strategies.

While the trends in ambient concentrations and outdoor exposure in populated areas have generally decreased, corresponding long-term trends in improving public health have not been documented. There is anecdotal evidence in the Los Ange-

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[6] A limitation in this approach is the use of observational data assimilation to constrain the forecasting model, which may preclude testing the forecast results with independent observations. The forecasting would have to be done without adjusting the model forecast with ambient data.

les area, for example, that people have experienced less short-term respiratory stress and ancillary eye or skin irritation (possibly from exposure to aldehydes or PAN in smog) as ozone concentrations have declined.

More quantitative evidence of the health effects of exposure to oxidants has come from intervention studies of a child cohort in the southern California that tracked children moving from high to low oxidant ozone exposure conditions and vice versa. Changes in respiratory measures such as lung capacity, ventilation rates, and respiratory stress for these children indicated adverse effects when children moved from low to high NO_2 concentration regimes and improvement when they moved in the opposite direction (e.g., Kunzli et al. 2003).

Time series studies of changes in adult health conditions with changes in ozone levels in urban areas, including Los Angeles, could provide insight into the effects of changes in subchronic or chronic exposure to ozone or photochemical oxidants; however, few such studies have been performed. Considerable effort has been expended on toxicology and epidemiology studies of ozone exposure. The evidence for acute respiratory and lung effects at approximately 80 ppbv, some of which are reversible, has been discussed in the EPA's recent Criteria Document (EPA 2006). The results also imply an apparent lack of a threshold for human response to ozone exposure. This result, along with other considerations, provided the rationale for the current U.S. 8-h average maximum daily limit of 0.075 ppm (EPA 2006).

An alternative to studying the relationship between ambient ozone and health for individual cities could be a comparative analysis for many cities, taking advantage of geographical, climate and pollution differences. Bell et al. (2004) performed such a study using 1997–2000 data from 95 U.S. cities. Their calculations indicate that the population risk of daily mortality from exposure to 24-h average ozone concentration by city ranges from 0 to 1.7% per 10 ppb of daily ozone increase. This value compares to a U.S. national average of 0.52% per 10 ppb ozone increase. Another recent long-term study of the large American Cancer Society (ACS) cohort by Jerrett et al. (2009) reports an association between ambient ozone and respiratory-related mortality. If the city-by-city results of Bell et al. (2004) and Jerrett et al. (2009) have appropriate population sizes for statistical significance, these results could suggest a relationship between ozone and acute mortality response by geographic location and chemical climate. This kind of statistical differentiation has not yet been reported.

Canadian investigators have reported a city-by-city assessment of health, ozone, and NO_2 trends between 1984 and 2000 (Shin et al. 2008). This analysis involved a space and time synthesis of non-accidental mortality and ambient pollutant concentrations for 24 Canadian cities. The results indicated an overall increasing trend in the running average of daily 8-h ozone concentrations that was associated with an overall decrease in annual averages of daily NO_2 concentrations. The association of year-to-year trends in ozone and NO_2 with mortality yielded some surprising results. Although the health risk of exposure to ozone appeared to remain unchanged, the risk associated with exposure to NO_2 increased as NO_2 concentrations decreased.

The reason for these trends is not known, but it could be related to four factors: (a) NO_2, which was identified by the investigators as an indicator of traffic-related emissions, is only a surrogate for the actual toxic agent (and while NO_2 concentration decreased, the actual agent did not), (b) high-risk populations may change with time, (c) the monitoring may not be an appropriate measure of actual exposure, or (d) the concentration-response curve may not be linear.

The above examples of studies relating changes in acute or chronic health effects to changes in exposure to ambient oxidants indicate the health effects of exposure to these substances. However, they do not constitute a complete accountability assessment as indicated by Fig. 3.2. Nevertheless, they could support design of more complete accountability studies, such as those that have been conducted for exposure to $PM_{2.5}$ (see Sect. 12.3.3).

12.2.4.2 Ecological Effects

Systematic multiyear studies of the effects of ozone or photochemical oxidants on natural ecosystems have not been conducted in North America. However, such effects have been investigated in controlled experiments on various vegetation species (see Chap. 6). Essentially all of the documentation of effects has been on vegetation (e.g., EPA 2006). Damage to crops, particularly leafy species such as lettuce and spinach as well as grapes, was documented in the eastern Los Angeles Basin by the 1950s, along with damage to evergreens in the nearby San Bernadino Mountains and in the Sierra Nevada Mountains (e.g., Miller et al. 1963). Agriculture began to move away from the Los Angeles Basin in the 1960s, so it has not been possible to determine if damage to agricultural crops would have been reduced as ozone concentrations began to decrease in response to the control measures that were taken. However, forests, including old-growth Ponderosa pine, in the nearby southern California mountains have not recovered extensively with reduction in ozone exposure (e.g., Miller et al. 1998).

Widespread effects of oxidants on vegetation, as measured by leaf discoloration of clover and other species, have been reported nationally, even at current relatively low summer concentrations of less than 100 ppbv (e.g., EPA 2006). Forest damage in various locations across the United States has also been reported based on surveys of trees and other vegetation. Studies of this kind, while showing effects in many locations, appear to be insufficient to quantify the response of vegetation to long-term changes in exposure to moderate concentrations of ozone or photochemical oxidants. Here again, long-term data are lacking to create a concentration-response relationship for exposure, or changes in exposure, for periods of a decade or more.

In conclusion, the risks of summertime exposure to ozone or photochemical oxidants for both humans and vegetation are well established in the literature for a range of ambient concentrations. However, the long-term effects of ozone on vegetation health remain uncertain, even for high ozone exposure conditions such as those that exist in southern California.

12.2.5 Lessons Learned

- *To what extent have the current ozone air quality plans followed a multipollutant framework?*
  Ozone is an indicator for the many highly reactive species involved in complex non-linear tropospheric oxidant chemistry. It may also be an indicator of other (multipollutant) photochemical oxidants that could affect humans and ecosystems. Since the 1970s, lowering precursor emissions have lowered ozone concentrations in most locations across North America. These emission reductions have been guided by theoretical considerations and by gradually improving air quality models that account for multipollutant interactions. Nevertheless, the observed reductions in ozone concentrations resulting from these management strategies are not completely understood. The ozone problem is a good illustration of the complexities of dealing with multipollutant systems on multiple spatial and temporal scales.
- *Given accurate knowledge regarding emission changes, are currently available tools able to assess the effectiveness of the management strategies adopted to reduce concentrations of each of pollutant or pollutant group?*
  The inadequacies of past air quality management strategies are reported in the literature. However, progress to date indicates that these strategies generally have been successful in reducing exposure to oxidants for humans and ecosystems. Weight-of-evidence indicates that short-term ground-level ozone concentration maxima are declining on a variety of spatial scales as projected by recent modeling calculations. However, the apparent increases in ambient ozone in the Toronto and Vancouver areas are notable exceptions to this generalization.
  If the trends do not follow projections, the tools needed to interpret these deviations are available, in principle. Changes in observed ozone concentrations have been compared with estimated changes in the ambient concentrations NO_x and VOC to see if these changes have been consistent with the expectations of decision-makers. However, the effectiveness of past actions to reduce precursor emissions has not been tested by thorough retrospective studies.
  Recent analyses of the effectiveness of measures taken to reduce ozone pollution both regionally and in urban areas of the United States, Canada, and Mexico City, show that it is possible to make quantitative comparisons of projected and actual precursor changes with observed ozone changes. Pursuit of such studies, as well as subsequent risk analysis, could be facilitated by requiring that design and implementation of performance evaluations studies be a part of future major control initiatives. Such studies should attempt, at a minimum, to verify the emission through exposure links in the accountability chain drawn in Fig. 3.2. In this way, the measurements, prospective modeling, and documentation of emission changes needed to establish accountability can be determined. However, given current uncertainties regarding many precursor emissions and an ozone monitoring system that has not been optimized for accountability assessment, it

is important to establish how capable the current system might be for undertaking this task.

- *Is current knowledge about environmental effects of ozone sufficient to quantify the effects of reducing ambient ozone concentrations on human and ecosystem health in North America?*
  The consequences of exposure to ambient ozone in humans have been investigated by various methods, and the effects, from respiratory morbidity to mortality, have been identified. In addition, effects of exposure to co-pollutants, including NO_2, organic nitrates, or other organic are suspected, but the evidence as reported in the literature is incomplete. Attempts to link improvements in public health with improving urban ozone air quality have relied on anecdotal data, combined with epidemiological investigations based on geographical differences in ozone exposure. These results have been sufficient to support analyses of health risks for goal setting. Some investigators believe that ozone is also an indicator of other toxic agents in photochemical smog, because investigations to date have not shown specifically that ozone is a meaningful indicator of human health or ecological responses to exposure to photochemical smog. With respect to multi-pollutant air quality management, risk assessment research could be broadened to incorporate additional measures of the effects of photochemical oxidants, such as NO_y and organonitrates.
  The effects of chronic exposure to increasing concentrations of ozone and associated co-pollutants on vegetation were well established by observations of vegetation damage in southern California during the 1950s–1960s and by more recent surveys of damage to agricultural crops and terrestrial vegetation. However, there is little knowledge at present for assessing how vegetation might respond to long-term reductions in ozone concentrations, as long-term improvements in terrestrial biota resulting from reductions in ozone exposure remain undocumented. Given current knowledge, one would expect damaged vegetation to recover over time, assuming that other factors are not involved, such as disease or climate change. Recovery has been difficult to establish for agricultural crops, because the production of crops vulnerable to ozone has been moved away from high ozone exposure areas, or it has been replaced by varieties that are resistant to ozone damage.
- *To what extent have multipollutant effects been recognized and accounted for in the evolution of management practice?*
  While the strategic focus of air quality management has been on ozone *per se*, early investigations of the effects of air pollution included consideration of a range of reactive intermediates including oxidants and toxic species in photochemical smog. Insufficient attention has been given to the measurement of precursors and oxidants other than ozone, including reactive nitrogen species, except for NO and speciated VOC. This lack of attention has created important gaps in the information needed to support complex model applications (e.g., NARSTO 2000).

  Air quality strategists assume (without proof from observations) that photochemical trace species decline as ozone levels decline. Systematic investigations of various trace species in smog have generally been too rare to document their presence and their changes over time. Studies that have been done in recent years have focused on species relevant to photochemical processing, such as OH and RO_x free-radical chemistry, or the uncommon nitrogen oxides, e.g., HONO, HNO_3, or N_2O_5. The health and ecological consequences of persistent exposure to these species have not been studied in urban settings, except perhaps historically in southern California.

12.3 Particulate Matter and Oxidant Chemistry

Current air quality goals for particulate matter focus on fine particle ($PM_{2.5}$) mass concentration. Since the ambient standards for $PM_{2.5}$ have existed for only about a decade and emissions compared with ambient concentrations are still being evaluated, longer-term trends rely on the PM_{10} measure of mass concentrations. Particle emissions need to account for both primary emissions and precursor gases such as SO_2, NO_x and certain VOCs, which oxidize in the atmosphere to produce particle mass. Oxidation of these precursors links particle chemistry with photochemical oxidant production. Historically, modeling and ambient concentration data for particle mass and composition have been used for design of reduction strategies. The projected results of these designs generally have not been verified retrospectively. Both primary and precursor emissions have trended downward since the 1980s, and ambient concentrations of PM_{10} and $PM_{2.5}$ have followed these trends. Trends in major components of $PM_{2.5}$ such as sulfate have compared favorably with reductions in SO_2. Trends in other major components such as nitrate or carbon are not well documented. Unlike the case of ozone, studies of particulate exposure have begun to differentiate between indoor, outdoor and activity based exposure. Documentation of changes in health response with changes in ambient $PM_{2.5}$ concentrations have been reported based on intervention studies and a few comparisons of epidemiological results over the period between the 1980s and present. The accountability chain for $PM_{2.5}$ has begun to approach qualitative closure as depicted in Fig. 3.2.

12.3.1 Evolution of PM Strategies

As indicated in the diagram in Fig. 7.1, photochemical processes not only create an atmospheric reservoir of reactive species including oxidants, but also their chemistry is closely related to particle formation in the atmosphere. On a mass or molar concentration basis, CP gases generally exist in substantially greater concentrations than particles. However, in recent years evidence has emerged that particles have a significant effect on humans, perhaps more so than the gases at ambient concentrations. Further, particles play a dominant role in visibility impairment across North America, as a visual index of air quality (McMurry et al. 2004). Airborne particles may be the most complex multipollutant constituent in the troposphere owing to their large number of sources, wide range of sizes, and their chemical composition.

Researchers have found that sulfate makes up a major fraction of sampled particles, especially particles smaller than a few micrometers in diameter. Measurements also have indicated the presence of nitrate in air, including a portion in fine particles. In addition to sulfate and nitrate, a third major component in fine particles is non-carbonate carbon. This fraction is composed of black (elemental) and organic carbon. Literally hundreds of carbonaceous compounds are present in the particles at varying concentrations from micrograms to picograms. Particles are also affected by photochemical reactions that result in reaction products that are superimposed on other chemical constituents, which can include soil dust, a wide range of metals from anthropogenic and natural sources, salt from marine origins, and waxy or humic carbonaceous material from vegetation, fragments of spores, pollen, bacteria and other cells. Although particulate matter is compositionally complex, the current weight-of-evidence mainly associates the health effects of exposure to particulate matter with the simple measure of mass concentration (both PM_{10} and $PM_{2.5}$). Associations between mass concentration and health endpoints are thus the metrics for guiding policy development. Consequently, current standards are geared toward reducing mass concentrations as opposed to being optimized for specific chemical constituents. Given the chemical complexity of airborne particles, which can vary as a function of source and with ambient chemical processing, the predominant common measurement used in epidemiological research on the health effects of particulate matter has been mass.[7] This approach assumes that all of the components of PM_x are equally toxic, although there is evidence (e.g., for metals, including lead, and diesel exhaust particles) that this may not be the actual case.

12.3.2 Air Quality Emission Reductions and Air Quality Trends

Strategies for reducing emissions responsible for particulate matter pollution have changed as air quality goals and standards have changed. The sources responsible for ambient PM vary with particle size. When the standard was based on TSP, the focus was on large particles because these dominate the total mass fraction. Consequently, the principal sources of concern were fugitive dust emissions from blowing soil dust, emissions from roadways, and emissions from certain industrial, mining, and construction activities. Later, the adoption of a PM_{10} ambient standard increased attention on sources responsible for smaller sized particles. Although PM_{10} mass is

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[7] Prior to the 1980, particulate air quality goals were established on a mass basis using the measure of total suspended particles (TSP), based on gravimetric determination of filter collection over 24 h. This measurement used a sampler collecting particles roughly ≤35 μm in diameter.

also significantly influenced by fugitive dust, contributions from combustion sources and from particles produced in the air form a more important mass fraction.

Efforts to reduce TSP and PM_{10} emissions from fugitive or "open" sources, either by permitting or by controlling dust, greatly reduced the mass concentrations of large particles (i.e., TSP) and brought most U.S. urban areas into compliance with the applicable NAAQS. However, recognition as early as the 1970s that very small particles were the agents probably responsible for the health consequences attributed to PM gave rise to efforts to reduce ambient concentrations of particles containing sulfate, certain carbon compounds (including the polycyclic aromatic hydrocarbons or PAHs), and trace metals. Concerns about exposure to trace metals led to a NAAQS for lead in the United States, however, national standards for ambient sulfate were not established. HAPs relevant to PM such as PAHs, and certain metals are governed by emission standards.

Visibility impairment is also a fine particle problem (McMurry et al. 2004). Efforts to improve visibility, such as the U.S. regional haze rule, require attention not only to primary particle emissions, but also to precursor emissions such as SO_2 and others that participate in the formation of secondary particles in the atmosphere. Thus, it has long been recognized that improving visibility requires a multipollutant approach.

In 1997, EPA established a NAAQS for $PM_{2.5}$ to address the health effects of fine particulate matter more directly. With this standard, increased attention has been given to primary emissions of fine particles from combustion sources, industrial operations, and open vegetation burning. This standard also required increased attention to precursor emissions such as SO_2 (which forms particles containing sulfate), NO_x (which forms particles containing nitrate), ammonia (which forms particles containing ammonium) and VOCs (particles containing organic compounds). Since the 1970s, major local and regional reductions in primary emissions of fine particles (including multipollutants such as the listed HAPs and metals) have occurred in fossil fuel burning power plants, in ferrous and non-ferrous metal production, and a variety of other sources. After the 1980s, reductions in particles containing sulfate, and to a lesser extent nitrate, have accompanied SO_2 and NO_x emission reductions in North America (e.g., note recent major emissions reduction initiatives listed in Table 8.1). Decreases in certain VOCs have accompanied reductions in motor vehicle emissions, as well as reductions in the petroleum and refining sectors and in industrial operations. In the industrial sector case, VOC reductions have resulted from initiatives focused on reducing the ambient production of photochemical oxidants. These initiatives have emphasized reducing emissions of the lighter VOC compounds, which are the majority of VOC by mass. Emissions of higher molecular weight VOCs (including aromatic compounds), which are important in forming $PM_{2.5}$, have not been addressed specifically.

Beginning mainly after 1990, information about the sources of primary particles has been limited to the total mass of these emissions. Historically, little information has been reported on chemical composition. This lack of information on speciation represents an important limitation on the development of multipollutant air quality management.

Sulfur dioxide and NO_x (see complexities of nitrate in Text Box 12.1) are primary precursors of secondary particle formation. Emissions of VOCs are important in the formation of fine particles and $PM_{2.5}$. Reductions in VOC emissions have resulted from improved control of mobile and stationary sources, improved exhaust catalyst performance, and better control of fugitive emissions. Given the relatively high importance of organic carbon in urban $PM_{2.5}$ and its suspected toxicity, issues remain concerning the emission of primary particulate carbon from combustion and the production of secondary organic aerosols from primary VOC emissions. Furthermore, the effects of potential changes of aromatic compounds in gasoline, and the significance of the unmanageable biogenic contributions to secondary organic aerosols from the oxidation of isoprene and terpenes, need to be better characterized.

Text Box 12.1 Shift in Partitioning of Oxidized Nitrogen with Sulfate Reduction

The interactions of sulfur oxides and nitrogen oxides in changing the inorganic portion of atmospheric particle composition are an important example of multipollutant chemistry affecting $PM_{2.5}$ levels. Changes in $PM_{2.5}$ (mass) concentration with sulfate reduction vary with changes in ammonium nitrate concentrations depending on seasonal climate, emissions and air chemistry. Southeastern Canada is particularly sensitive to changes in nitrate partitioning since particulate nitrate (pNO_3) is a relatively large fraction of $PM_{2.5}$ with sulfate.

Formation of pNO_3 is a complex process related to NH_4NO_3 equilibrium. In addition to HNO_3 and N_2O_5, which are oxidation products of NO_x, ammonia (NH_3) is required. The level of pNO_3 is sensitive to ambient levels of sulfate (SO_4^{2-}), and relative humidity. Sulfate has an influence due to the preference of NH_3 to react with acidic SO_4^{2-} before contributing to fine nitrate formation. Ansari and Pandis (1998), West et al. (1999) and Blanchard et al. (2007) discussed the interplay between NH_3 and SO_4^{2-} in eastern North America. The former used the 'gas ratio' as a sensitivity parameter to assess how pNO_3 changes in response to changes in sulfate or ammonia. Gas ratio (GR) values for selected locations in southern Ontario and Quebec in the early 1990s indicated that there could be situations in which the total fine particle mass ($PM_{2.5}$) would respond non-linearly or even negatively to changes in SO_4^{2-} and/or NH_3 (i.e., potential $PM_{2.5}$ increases when SO_4^{2-} is decreased).

12.3.2.1 Trends in Ambient Particle Concentrations

Methods for monitoring atmospheric particles in North America have evolved since these measurements began in the 1970s. Prior to 1980, measurements concentrated almost exclusively on TSP, although a few observations of PM mass by size fraction were also made (e.g., EPA 1981; EPRI 1987; Hidy 1994). In the 1980s, systematic monitoring was begun in the United States to characterize a fine particle fraction ($PM_{2.5}$) and an inhalable or "thoracic fraction" (PM_{10}) at a number of urban locations for research purposes.

After the PM_{10} standard was adopted in the 1980s, PM_{10} mass concentrations were monitored routinely in the United States; however, urban measurements of the chemical composition of PM or $PM_{2.5}$ mass were not conducted. In Canada, TSP monitoring was updated at this time with establishment of the National Air Pollution Surveillance (NAPS) dichotomous sampler network, which provided additional information on PM mass as a function of size. Consequently, the longest (urban) continuous time series for $PM_{2.5}$ and $PM_{10\text{-}2.5}$ (PM_x) in North America exists for several Canadian cities. Also in the 1980s, the Interagency Monitoring of Protected Visual Environments (IMPROVE) network was established in the United States in response to concerns about rural visibility. The IMPROVE network has been reporting particle mass concentrations and chemical composition at a growing number of sites since then. In the 1980s, Mexico also established PM_{10} monitoring at selected sites, especially in Mexico City (e.g., Molina and Molina 2002). As a result of these efforts, PM_{10} observations are available at many urban and rural locations in North America since the late 1980s. By the year 2000, observations of $PM_{2.5}$ mass concentrations and had been established across the United States and Canada, and at certain sites in Mexico. By 2002, measurements of chemical composition (sulfate, nitrate, and other species) were also added (see Chap. 10 and Appendix B, www.narsto.org).

National trends in PM_{10} concentrations in the United States have shown a steady decline in concentrations since the 1980s (EPA 2008). These downward trends have varied somewhat by region, but in the United States most urban areas, except in California, were in compliance with the PM_{10} NAAQS by the early 1990s. In Mexico City PM_{10} concentrations in the metropolitan area have experienced dramatic reductions, which are associated with reductions in primary emissions from open sources and from reductions of precursor emissions from major sources (Table 12.3; Fig. 12.5). Canadian data for 24 h average $PM_{2.5}$ concentrations show urban concentrations have been in the range of 5–35 μg/m^3. The Canada-wide $PM_{2.5}$ standard

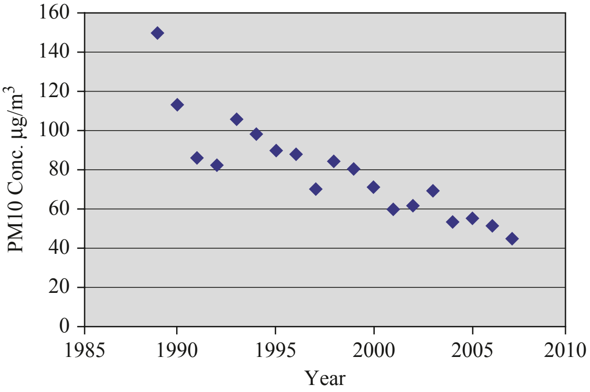

Fig. 12.5 Trends in annual average PM_{10} concentrations from five stations in the Valley of Mexico. (Source: Secretaria del Medio Ambiente del Gobierno del Distrito Federal, Sistema de Monitoreo Atmosferico 2008)

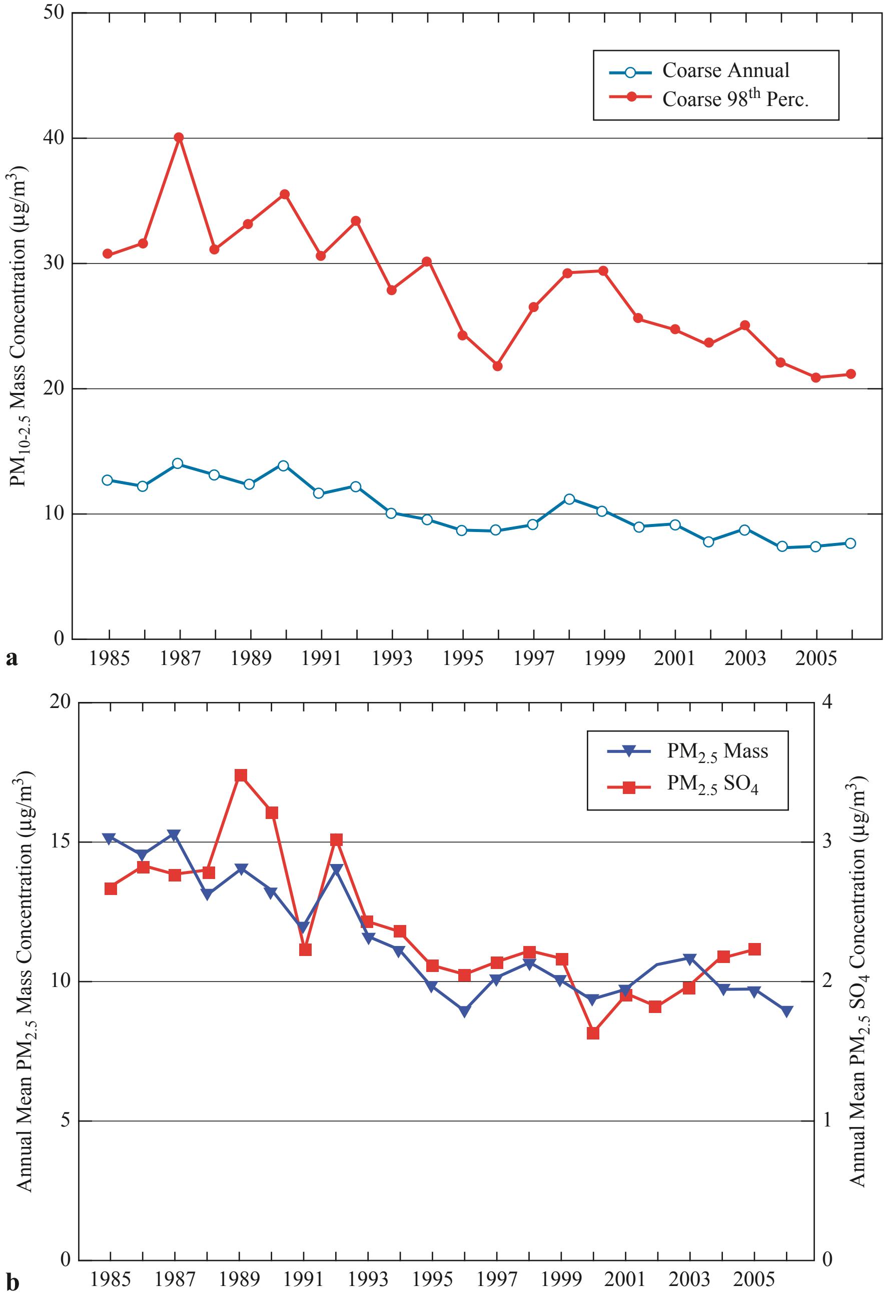

Fig. 12.6 Trends in Canadian PM_x data from dichotomous samplers between 1985 and 2006. (**a**) PM_{coarse}, $PM_{10\text{-}2.5}$ and (**b**) $PM_{2.5}$ and $sulfate_{10\text{-}2.5}$. The samplers are located mainly in southeastern Canada. (Source: Canada, 2011)

(CWS) is 30 μg/m^3 for the 98th percentile of measurements (averaged over three consecutive years). In terms of trends, one can infer from the data in Fig. 12.6a, b that PM_{10} concentrations in southern Canada, where the samplers are located, have also declined steadily since multi-site monitoring started in 1985. The figure also shows that there have been relatively steady reductions in the sulfate fraction of $PM_{2.5}$ as a result of SO_2 precursor emission reductions in both Canada and the United States.

In the United States, $PM_{2.5}$ concentrations declined nationally by about 14% between 2000 and 2006 (EPA 2008). Urban data indicate that trends differ geographically depending on local and regional conditions. For example, east of the Mississippi River these changes have been influenced by reductions in primary sources and in regional scale $PM_{2.5}$ precursors (EPA 2008). Over the longer term, trends in regional $PM_{2.5}$ concentrations documented by the IMPROVE observations have been mixed reflecting variations in rural-regional conditions (e.g., McMurry et al. 2004).

The Southeastern Aerosol Research and Characterization (SEARCH) network provides another example of long-term regional trends in $PM_{2.5}$ mass concentrations. The network, which has been operating since 1999, consists of eight paired urban and neighboring rural or suburban sampling sites (e.g., Hansen et al. 2003; Edgerton, personal communication). Results for a six-year period from 1999 to 2006 are shown in Fig. 12.7. The SEARCH trends indicate declining concentrations at the urban sites (Atlanta, Georgia and Birmingham, Alabama, for example)

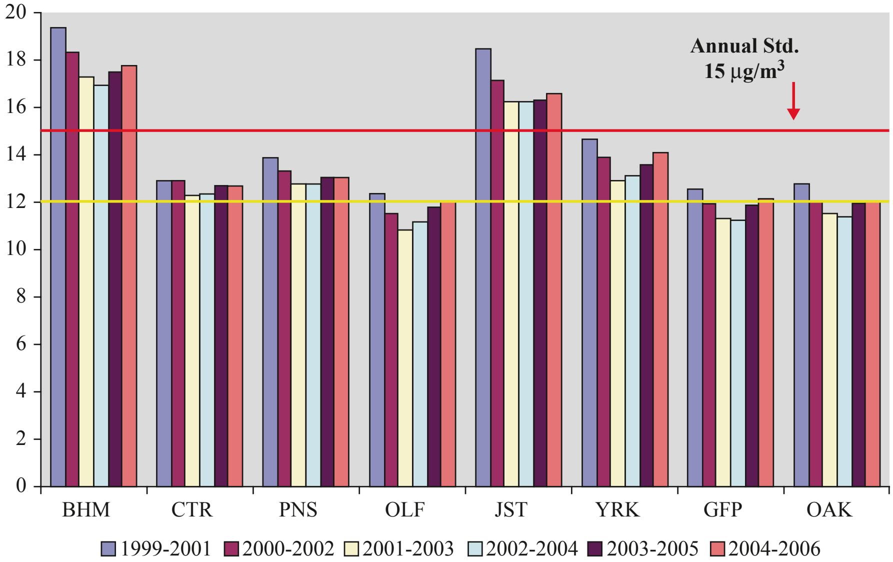

Fig. 12.7 Annual average $PM_{2.5}$ concentrations from the SEARCH network in the southeastern United States by location. *JST* (Atlanta), *BHM* (Birmingham), *YRK* (Yorkville-rural), *CTR* (Centreville, Alabama-rural), *GFP* (Gulfport, Missisippi), *OAK* (Oak Grove, Mississippi-rural), *PNS* (Pensacola, Florida), *OLF*, (Pensacola-suburban). (Courtesy of E. Edgerton)

through 2003 but a rise after this year. This behavior is less obvious at the rural sites, except for Yorkville, Georgia. The reasons for the apparent trend reversal are not clear. However, this example provides a good example of how regional circumstances may differ from national trends.

12.3.2.2 Chemical Constituents of $PM_{2.5}$

Regional variations in $PM_{2.5}$ composition are governed by differences in emissions and meteorology. In eastern North America, the sulfate component of PM_x has a strong regional character that depends on meteorological factors and the locations of major SO_2 sources (e.g., Hidy 1994). The carbon fraction, on the other hand, has a combined local and regional character, with important local influences from both organic and black carbon. The carbon fractions of $PM_{2.5}$ have only been measured recently by the U.S. STN program, the expanded IMPROVE network, and the NAPS speciation monitoring across Canada. In the United States, the SEARCH regional program has obtained a relatively long-term record of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ composition at the eight sites, including the two carbon fractions (organic and black carbon). The SEARCH data set provides a relatively long-term record (1999–2011) of urban and rural PM characteristics, which together with meteorological and pollutant gas data, has been valuable for use in health studies and decision making on $PM_{2.5}$ attainment and visibility improvement in the Southeast (e.g., Klemm and Mason 2000; Blanchard et al. 2006 and VISTAS [http://www.vistas.sesarm.org/links.asp{accessed March, 2009}]).

In general, long-term trends in urban sulfate and nitrate concentrations are poorly documented across North America. For the case of sulfate, measurements using different TSP, PM_{10} and $PM_{2.5}$ filter-based sampling and analytical methods are available for some cities in the United States as far back as the 1950s. However, the differences in sampling and analytical methods, combined with a poor record of emissions, preclude quantitative comparisons of changes in this PM component with changes in SO_2 emissions. More recent self-consistent data for rural areas is available from the IMPROVE network and the CASTNET system in the United States as well as from CAPMoN and NAPS in Canada. Some insight on regional trends can be obtained for 1989–2000 period from CASTNET monitoring in the United States and the CAPMoN sites in Canada (e.g., McMurry et al. 2004). As an example, Fig. 12.8 shows the change in SO_2 emissions in the eastern United States in comparison with ambient SO_2 measurements and 24-h average sulfate measurements. The decreases in ambient SO_2 and SO_2 emissions decrease over the network area are approximately 30%, but the decrease in ambient sulfate is about 23%. Over the same time period, nitrate concentrations show no systematic change. Similar trends have been observed in eastern Canada at the CAPMoN sites (Table 12.5). The national average concentration trends for Canada, as indicated by the NAPS network, are shown in Fig. 12.6b.

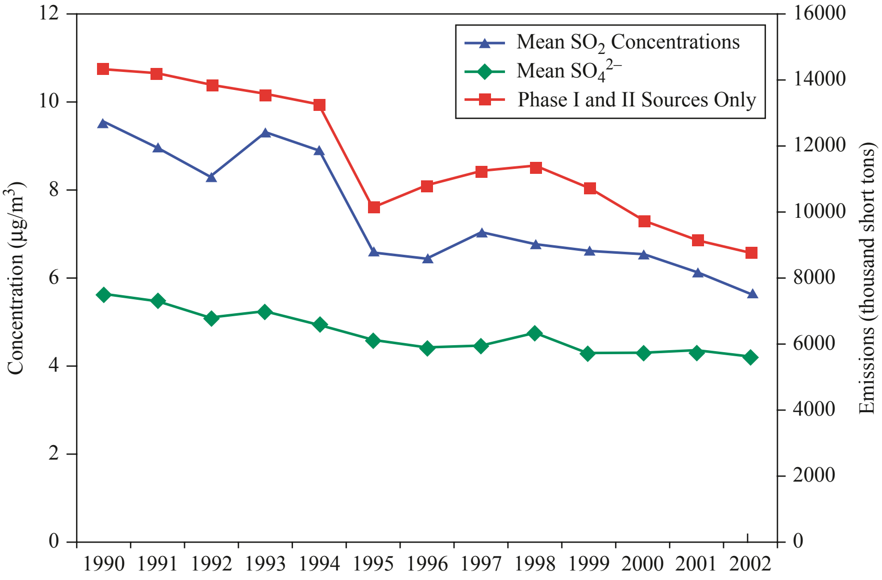

Fig. 12.8 Trends in 24-h filter-based average sulfate compared with SO_2 emission change and ambient SO_2 concentration change from the CASTNET monitoring network, located mainly in the eastern United States. (EPA 2002b)

From 1990 to 2004 there was nearly a 5 million ton reduction in SO_2 emissions for eastern North America. Over this same time period, NO_x emissions increased slightly at first and then started to decrease in about 1998. These trends have provided an opportunity to assess whether or not these SO_2 controls, which decreased ambient $SO_4^=$ and SO_2 concentrations and sulfate deposition, had the unintended consequence of increasing particulate nitrate. Percent changes in concentrations from the CAPMoN data comparing the five years before and after the SO_2 emission reduction are shown in Table 12.5. Unbiased estimates of fine particle nitrate (fNO_3) in the cold months can be calculated from these data, based on the assump-

Table 12.5 Percent change in Canadian Air and Precipitation Monitoring Network (CAPMoN) cold season concentrations of HNO_3, NH_4, NO_3, SO_2, SO_4, fNO_3 and cNO_3 between 1988–1993 and 1996–2001. (Source: EC 2008b)

Location	HNO_3	NH_4	NO_3	SO_2	$SO_4^=$	fNO_3	cNO_3
Longwoods	−22.7	3.2	12.5	−30.2	−23.2	48.7	−42.0
Egbert	−19.1	−10.2	5.0	−37.0	−25.0	17.9	20.4
Chalk River	−13.5	−5.1	55.7	−38.7	−26.1	143.1	17.8
Sutton	−21.6	−8.3	37.7	−41.8	−28.1	133	−18.4
Algoma	2.6	0.3	50.4	−38.8	−24.4	78.7	18.9
Chapais	−3.4	−13.0	148	−49.8	−33.6	1790	111
ELA	−0.7	−3.0	39.9	−31.9	−21.4	61.3	14.6
Kejimkujik	−21.7	−21.4	32.4	−37.0	−29.3	239	32.1

tion that all $SO_4^=$ is in the form of ammonium sulfate and that the remaining particle ammonium is in the form of ammonium nitrate. These calculations indicate that increases in cold-season fNO_3 for these time periods ranged from 18% to almost 1800%, depending on location. The largest increases were found in areas where pNO_3 tends to be low, such as northern Quebec (Chapais) and Nova Scotia (Kejimkujik). Table 12.5 shows that sulfur, both as a gas (SO_2) and as fine particles ($SO_4^=$), decreased relatively uniformly across the area. Total sulfur decreased by an average of 35%, which is consistent with the relative size of the eastern North American SO_2 emission reduction between the two periods, which was about 32%.

Additional CAPMoN measurements included in Table 12.5 indicate that the increase in fNO_3 was not due to increased NO_x emissions (or to more nitrogen in the atmosphere), but to a shift in its distribution. As mentioned previously, NH_3 reacts preferentially with sulfate. Thus, the “free NH_3” resulting from the reduction in $SO_4^=$ concentrations led to more of the gas-phase nitrogen (i.e., HNO_3) shifting to the fine particle phase. This is evidenced by the decrease in HNO_3 at all the sites. Coarse particle nitrate (cNO_3), which can form when HNO_3 reacts with the crustal elements found on larger particles, also decreased at several sites. The increases in fNO_3 and percent decreases in HNO_3 do not balance, however. This imbalance implies that shifting HNO_3 to fNO_3 through the increased availability NH_3 could result in greater export of oxidized nitrogen from areas of high concentrations to lower concentrations during the cold season.

Since carbon is a large fraction of PM_{10} and $PM_{2.5}$, one would expect that its control through reductions in emissions from the transportation sector, for example, would be demonstrated readily in ambient data or emissions records. However, routine measurements of the carbon content of PM and its chemical composition are not available for any extended periods of time to allow an accounting of this component.

The relationships between past or projected PM emission changes and particle mass concentration and composition have been analyzed for design of management strategies using both source-based models and receptor models. In the 1970’s local modeling for particles adopted several schemes to address projections from point sources and urban source mixes (e.g., Zanetti 2003). Eulerian grid models on urban to regional scales came of age in the 1980s with acid rain studies, and concern for airborne sulfate. (e.g., Hidy 1994; Zanetti 2003). Multicomponent models for $PM_{2.5}$ composition evolved into codes such as the CMAQ (Chap. 9) in the 1990’s. The reliability of projected reductions in ambient $PM_{2.5}$ concentrations has not been tested retrospectively, as yet for these complex models. However, the calculations from models have been consistent with the observed trends in the concentrations of sulfate (and to a lesser degree volatile nitrate and a portion of carbon) and with deposition of acid forming species.

Receptor modeling also has been used for evaluating source-ambient particle relationships in some cities and for some regional case studies. This approach has been applied in order to establish links between the sources of some $PM_{2.5}$ components and apparent health effects (e.g., Thurston et al. 2005; Grahame and Hidy 2007). If appropriate observations are available, the receptor models can be used, in principle, for retrospective analyses of change, and for assessing accountability between changes in primary particle emissions and ambient particle concentrations and composition, using appropriate source tracers or tracer inferences (Chap. 9). The limitations of this approach are noted in the reviews of McMurry et al. (2004), NARSTO (2005), Grahame and Hidy (2007) and Solomon et al. (2008).

The above examples summarize some of the analyses that have been conducted to characterize the relationships between the quantity and composition of PM_x emissions and in ambient PM mass concentrations and composition. Their ability to quantify long-term trends in particles remains to be tested further with newer ambient data. This comparison will be limited by ambiguities in primary particle and precursor emissions, and in the models themselves, through their incomplete descriptions of aerosol chemistry. Accountability analyses of PM_x will thus continue to require evaluation of the "weight of evidence" for documenting emissions to ambient air quality changes.

12.3.3 Health and Ecological Effects of PM Exposure

Like other regulated air pollutants, outdoor concentrations of particles represent only a surrogate for actual exposure, which depends on the time spent indoors and outdoors, the activity patterns of exposed individuals, the kinds of spaces they occupy, and the infiltration of ambient air into these spaces (see also Chap. 5). There have been some investigations that quantify exposure of a group of subjects based on indoor and outdoor measurements combined with information from personal exposure monitors. These studies have shown distinct differences in exposure to particles by mass concentration and composition depending upon the environment occupied by and the activity patterns of the subjects (e.g., Ozkaynak et al. 1996; Hidy et al. 2000). These studies found that ambient concentration, as measured by fixed outdoor monitoring sites, was an uncertain surrogate for indoor or activity-based exposure—except, perhaps, for sulfate. This finding differs from the results of the PTEAM study in Riverside California (EPA 1996), which rationalized the use of outdoor monitoring as a surrogate for PM exposure based on separation of the indoor and outdoor source components. Some health studies have attempted to decouple the signals from $PM_{2.5}$ of ambient and non-ambient origin and have shown there are clear associations between health effects and ambient concentrations of PM (Ebelt et al. 2005). This work supports the assumption that $PM_{2.5}$-health response is "universally" related to community-monitored $PM_{2.5}$ mass and composition, and it is used to support the design assumptions of a variety of health studies in the literature. It also supports the basic conclusion that reducing ambient mass concentrations of $PM_{2.5}$ results in improved public health ("for reducing risk, less is better").

A substantial body of research by epidemiologists and toxicologists has provided evidence of a relationship between exposure to inhalable PM and certain human health endpoints. Since the 1970s, most health-related research on the effects of exposure to PM_x has focused on establishing a relationship between ambient mass concentration of PM_x and health indicators and in the development of concentration-response relationships to express the health consequences of this exposure (e.g., EPA 1996, 2002a, 2005; EC 2008a). Over time, the nature of these concentration-response relationships changed as it became clearer that the size of atmospheric particles was an important factor in explaining PM_x health effects. This understanding has driven the evolution of particle size and mass-based standards (e.g., EPA 1996, 2002a). The current U.S. $PM_{2.5}$ standard is mainly supported by population-based studies of the relationship between mortality and ambient concentrations of PM in this size range (e.g., EPA 2001, 2005). Concentration-response relationships also have been used in Ontario and across Canada in an assessment of the risk of exposure to mass-based $PM_{2.5}$ concentrations. The results of this assessment were used to develop the Canadian national ambient standard (CWS) for fine particles. An analogous approach has been used to support the ambient standard for PM_{10} in Mexico. This work continues, and recent improvements in epidemiological methodologies suggest that new analyses will provide insight into the relationships between $PM_{2.5}$ mass and composition exposure and population risk of adverse health consequences (e.g., Dominici et al. 2007; Tolbert 2007; Reiss et al. 2007).

Until recently, there has been much less research on concentration-response relationships for particle physicochemical properties in addition to size-resolved mass concentration. There is some evidence that specific chemical components of PM might be more toxic than others. These components include certain metals, carbon, and certain organic compounds (such as various HAPs) and $PM_{2.5}$ associated with diesel emissions (cf. Mauderly and Chow 2008). There is also concern that inhalation of ultrafine particles of diameter less than 0.1 μm could have greater negative health consequences than the larger particles contained in a $PM_{2.5}$ size cut. However, this evidence is not strong enough to implicate any specific PM_x component or $PM_{2.5}$ size range as the principal agent or agents of concern or to remove any of these PM_x characteristics from the list of suspects. Thus in spite of recent progress in understanding the health effects of particulate matter, air quality standards still rely on a size-mass concentration standard as an exposure surrogate.

Despite the extensive research on human health effects of PM_x, only a few analyses have been reported relating actual trends in improvement of human health to declining ambient particle concentrations (see also Chap. 5). Until recently, this kind of evidence had come from "natural experiments" or intervention studies where a rapid reduction in PM_x concentrations has occurred within a specific airshed. These incidents demonstrate that health benefits are observed in affected populations when there are significant rapid reductions in PM_x exposure (e.g., HEI 2003; Schlesinger et al. 2006). Examples of such incidents include (a) the Utah steel mill closure (Pope 1989); (b) the reduction in sulfur in residual oil and diesel fuel in Hong Kong (Hedley et al. 2002); (c) the banning of residential coal combustion in Dublin, Irelend (Clancy et al. 2002); and (d) the widespread shutdown of copper smelters in the U.S. Southwest (Pope et al. 2007).

The Utah study examined PM-mortality associations over a four-year period that encompassed a one-year closure of a steel mill in the Utah Valley. The closure led to a large reduction in pollution emissions, and a corresponding improvement in air quality persisted until the facility was reopened. Filter-based measurements of PM composition within the Utah Valley during the time the mill was operating confirmed that the filter samples were rich in metals having high inflammatory potential (e.g. Ghio 2004).

The Hong Kong example results from an action taken by the government to limit the sulfur content of the fuels used in power plans and vehicles. Sulfur dioxide and sulfate concentrations declined immediately. For a two-year period following the action, SO_2 concentrations within the city declined by 15–23% before finally returning to pre-intervention levels. Other pollutants (NO_2, ozone and PM_{10}), however, showed no clear declines. Respiratory health and mortality were monitored before and after the intervention (Hedley et al. 2002). Both the prevalence of respiratory symptoms and cardio-respiratory mortality declined after the reductions in sulfur content. Although the study suggests health benefits for reduced sulfur emissions, it contains some inherent ambiguities, including the large decline and subsequent rebound of SO_2 concentrations during the study period. Later, Hedley et al. (2006) found that in addition to the sulfur reductions the intervention reduced ambient vanadium and nickel concentrations by 90%. This latter observation points to an association of sulfate combined with certain metals with apparent health effects, as noted in other studies (e.g., Grahame and Schlesinger 2007).

The third example is the Dublin case in which the use of bituminous coal for domestic heating was banned in the fall of 1990. This intervention resulted in an immediate reduction in ambient black smoke and SO_2 concentrations. Wintertime concentrations of black smoke, an indicator of fine particle concentrations, declined from 80 to 20 $\mu g/m^3$. Clancy et al. (2002) showed that cardio-respiratory mortality for the three years following the ban fell compared to the three years preceding it. Given the lack of direct measurements of mass concentration and the uncertain nature of the black smoke measurements, it is not possible to assign the observed health effects to a specific pollutant.

The study of Pope et al. (2007) focused on the possible effects of a region-wide reduction in SO_2 emissions and sulfate concentrations in the U.S. Southwest during a 1967–1968 copper smelter strike. Pope et al. inferred a reduction in monthly mortality across the region (influenced strongly by urban centers) due to emission reductions during the strike. They theorized that the mortality reduction was associated with reductions in ambient sulfate concentrations (as a marker for $PM_{2.5}$) over a very large region. Particle mass concentrations were measured during the period as TSP, but no trends were identified with this measure of particulate concentration. The results of this study are also ambiguous given evidence of sulfate effects (e.g., Reiss et al. 2007), and inconsistencies in the decline in ambient sulfate concentrations across the region (e.g., Hidy 2007).

Of more importance to accountability, however, are recent assessments of the health benefits of the national-scale reductions in PM_x that have occurred over the past few decades. Key examples are the analyses of Laden et al. (2006), Pope et al. (2009), Jerrett et al. (2007) for PM, and Fischer et al. (2009) for black smoke. These studies begin to establish a relationship between ambient PM concentrations and changes in health effects for exposed populations. Laden et al. (2006) examined a

1990–1998 follow-up of an adult cohort study of PM and health for six U.S. cities during the 1970s and 1980s. The Laden study provides perhaps the first evidence of health improvement associated with reductions in ambient $PM_{2.5}$ concentrations. Their results indicate that the estimated adjusted-rate ratios for total mortality as a function of $PM_{2.5}$ concentrations in all six-cities declined from the 1974–1989 period to 1990–1998. During this time, $PM_{2.5}$ mass concentration in the six cities declined by 0.43 to 1.06 $\mu g/m^3$ from 1980–1985 to 1990–1998. Recently, Pope et al. (2009) have reported that apparent changes in ambient $PM_{2.5}$ concentrations between 1980 and 2000 are associated with improvement in life expectancy in a sampling of 51 U.S. cities. Both the Laden et al. and Pope et al. studies have technical limitations that have been debated in the literature. However, they offer encouragement to investigators and decision-makers and support the use of innovative methods for relating ambient concentration changes to improved public health endpoints.

The few long-term trend analyses are not necessarily divergent, but do point out the ambiguities of interpreting PM_x mass concentration (or inferred composition)-health response relationships, and the apparent differences in toxicity of PM_x components. Studies of Jerrett et al. (2007) and Fischer et al. (2009) also show public health improvements with reductions in ambient concentrations of PM_x. The work of Jerrett et al. (2007), in particular, bears directly on the association of health improvement with particulate air quality improvement. Jerrett et al. followed up the American Cancer Society (ACS) cohort with an analysis of the relative health risk of $PM_{2.5}$ and sulfate exposure in 51 U.S. cities covering five time periods between 1982 and 2000. They reported that relative risk of cardiopulmonary disease declined as sulfate concentrations declined. However, they found that relative risk increased for $PM_{2.5}$ exposure during the same time period. This result implies that the non-sulfate fraction of $PM_{2.5}$, which was presumably unchanged during the same time period, may have increased and that this increase may have enhanced the apparent toxicity of the particles. The study by Fischer et al. (2009) examined the relation between ambient PM, as inferred by black smoke observations, and mortality for the Netherlands. The study did not demonstrate a conclusive relationship between the two measures, but it did not preclude a long-term association between them.

Questions regarding the management of the organic carbon component of ambient particulate matter present a major challenge to regulators. The chemistry of this component is extremely complex and incompletely understood, as it involves criteria pollutants, HAPs, other undocumented organic emissions, and the myriad of secondary, semi-volatile substances that are formed as these substances are oxidized in the atmosphere. How these reactions might affect the biological activity of PM is unknown, and it is a major challenge to multipollutant air quality management.

The lack of observations of $PM_{2.5}$ for periods longer than a decade, particularly in relation to health effects, creates a barrier to a more complete multipollutant air quality management practice for this pollutant. It also limits our ability to integrate management of $PM_{2.5}$ and photochemical oxidants, such as ozone, on the basis of relative risk. Recent U.S. criteria documents cite clinical and human-exposure studies involving both ozone and PM_x, but these experiments do not indicate whether the health effects of combined exposure to these substances is additive, synergistic, or antagonistic. Nevertheless, the recent reported results of Jerrett et al. (2009) derived from the ACS cohort make the distinction between the effects of $PM_{2.5}$ and ozone on health response.

Beyond their contributions to acidification, nitrification, or the deposition of toxic metals, no significant detrimental effects of exposure to ambient PM at contemporary concentrations have been reported for ecosystems. The potential for adverse ecological effects probably results from the deposition of particles on vegetation or deposition to water bodies. These effects have been investigated primarily through the use of biomarkers, such as lichens, and in some cases through analysis of dustfall on leaves.

In the United States, visibility is an important air quality related value, particularly in pristine areas. Visibility impairment has been tracked in the United States and Canada using visual range observations, and in the United States by light-scattering observations in remote areas as part of the IMPROVE network (e.g., McMurry et al. 2004). Visibility is estimated from these latter measurements using a relationship that relates visibility to light scattering and the fine particle mass concentration of various chemical constituents. Visibility improvements have been observed to follow from control of particulate emissions and SO_2, and in the United States, a formal commitment to improve visibility in pristine areas over the next half century is included in the regional haze rule (EPA 1999; http://www.epa.gov/ttn/oarq/t1/factsheets/9wsoit_fs.pdf).

12.3.4 Lessons Learned

- *To what extent have the current PM air quality plans followed a multipollutant framework?*
  Important progress has been made on the characterization of the major chemical constituents of PM_x. However, this knowledge has not led to unequivocal identification of the specific chemical component or components responsible individually or in combination for the observed effects of PM_x exposure on health. Part of the problem is the complex multipollutant character of ambient particles and the volatility of some PM constituents. As a result of this volatility, the chemical composition of particles as sampled may not be representative of their composition in the free atmosphere or in the respiratory systems of exposed individuals. The monitoring methods for PM_x are ambiguous for taking volatility into account. Thus, the measured size-specific mass concentration as an exposure indicator remains problematic for health impact. The principal exceptions to this rule are for exposure to particles containing thermally stable constituents such as sulfate, lead, and other toxic metals.

- *In the light of knowledge about emission changes, do the available tools provide confidence in the ability to assess the effectiveness of the management strategies adopted to reduce concentrations of each of pollutant or pollutant group?*

  Trends in particulate mass concentration have been documented for differing size regimes for some time; however, the record for fine particles, such as $PM_{2.5}$, is fairly short. The PM_{10} record is long enough in North America that we can be confident that this particle fraction has indeed declined in most locations where measurements have been taken. However, the record for urban $PM_{2.5}$ concentrations is probably too short to be confident that the apparent reductions observed in the United States and Mexico are due to reductions in emissions, meteorological variability, or both. In Canada, the record is longer, and observations since 1985 suggest a decline in $PM_{2.5}$ concentrations resulting from reductions in primary sulfur oxide emissions. There is evidence of reductions in airborne sulfate across parts of the United States and Canada resulting from reductions in SO_2 emissions in both countries. However, such "definitive" evidence is absent for other major constituents such as nitrate and carbon, which are more difficult to measure and model and have been influenced by smaller emission reductions than SO_2.

  The relationship between changes in PM_x mass concentrations and changes in precursor emissions is complicated by the fact that ambient PM includes both primary emissions and particles formed by chemical reactions in the atmosphere involving gaseous precursors. The importance of primary emissions and secondary particle formation also varies with particle size. Most of the reductions in $PM_{10\text{-}2.5}$ concentrations have resulted from reductions in primary emissions. Reductions in primary particle emissions have been achieved for stationary and transportation sources and for some fugitive sources such as road dust (although wildfire emissions have probably increased). Reductions in visible plumes of dust and smoke from transportation and stationary sources, as well as improvements in visibility measures, provide anecdotal evidence of decreases in PM_x across North America. However, the weight of evidence from ambient measurements and changes in primary emissions of fine particles is probably insufficient to be confident that changes in the fine particle fraction of PM projected for past PM reduction strategies have been achieved other than for sulfate and some metals such as lead. It is likely that carbon from motor vehicles and other sources has declined both in Canada and, after the 1980s, in the United States. Some evidence of this change be found by comparing early data (e.g., IMPROVE) with recent observations; however, similar data for urban locations are generally not available.

- *Does knowledge about environmental effects give confidence in the ability to assess whether changes in regulated pollutant indicators will result in improved public health and ecosystem health in North America?*

  Our knowledge of human response to exposure to particulate matter is complicated by difficulties in determining indoor and outdoor exposure and dose. Epidemiological studies have generated concentration-response parameters for estimating the health effects of exposure to particles by relating human health response to changes in outdoor particle concentrations. This information is supplemented by a variety of toxicological studies that have exposed biological tissue, whole animals, and human subjects to various kinds of particles. These studies have added insight into possible injury mechanisms for some particulate components. Two recent epidemiological studies looking at large and/or important cohorts in the United States have provided evidence that gradual changes in PM_x mass concentrations during the past 25 years have resulted in reduction in mortality rate. Evidence that reductions in ambient PM_x mass concentrations result in health improvements has also come from intervention experiments that have documented changes in population health with sudden reductions in source emissions. Yet due to the nature of PM_x and its sources, these interventions are also associated with reductions in other ambient pollutants. Consequently, it cannot be stated with full confidence that the observed benefits resulting from these interventions are due entirely to the change PM_x concentrations, as opposed to changes in the complex mixture of gases and particles associated with them.

- *To what extent were multipollutant effects recognized and deficiencies accounted for in the evolution of management practice?*

  The importance of grouping particle properties by size, physical, and chemical characteristics has been reinforced by research conducted over the last decade. Research on exposure-health-response linkages continues, but our knowledge has not reached a level where a multipollutant air quality management approach focusing on specific toxic components of ambient particles could be implemented with confidence.

  The multipollutant nature of airborne particles and particle exposure has long been known and has been an underlying factor in air quality management. The ambiguities in determining both detailed characteristics and complex composition of particles, and the relative health risks associated with these properties continues to lead to uncertainties regarding the level of risk reduction that might result from particle mass reductions based on a single constituent. Management practice has taken into account, to some extent, the effects of particle size, (i.e., the evolution of the mass concentration standard from TSP to PM_{10} to $PM_{2.5}$), but it has yet to deal with the apparent variability in toxicity as a function of specific chemical composition. Further advancements in specificity of PM_x management practice will depend significantly on new knowledge gained from studies of how the multipollutant character of PM_x evolves in the presence of pollutant gases and of the significance of this evolution to health effects.

12.4 Acid Deposition

During the 1980s, deposition of strong acids to vulnerable ecosystems became an important air quality issue in Canada and the United States. Sufficient evidence of damage to aquatic and terrestrial ecosystems in parts of the countries motivated the

Canadian and U.S. governments to legislate regional control measures for sulfur and nitrogen oxides in the 1990s. Deposition of these species and chemistry and biological productivity in some vulnerable surface waters and affected forests have been measured continuously since the 1980s. The results of the measurements have at least qualitatively verified the projections of regional deposition and watershed chemistry models used to design management strategies. These results have shown that most observed surface waters have responded to reduction in sulfate deposition, but their response to nitrate deposition is less clear. While water chemistry has improved, aquatic biota recovery from acid deposition has been much slower. Recovery of acid-sensitive terrestrial ecosystems measured, for example, by soil chemistry and red maple and certain evergreen health remains ambiguous. These results indicate at least a partially complete accountability sequence as depicted in Fig. 3.2.

12.4.1 Evolution of Deposition Reduction Strategies

The oxidation of SO_2 and NO_x in the atmosphere produces strong acids if these chemicals are not otherwise neutralized *in situ.* This section complements the earlier discussion in Chap. 6 as an example of multipollutant air quality management involving the atmospheric chemical processes that affect SO_2 and NO_x emissions, aquatic and terrestrial acid-base chemistry, and ecological effects.

Research on the effects of acid deposition has concluded that strong acids are not the only concern with respect to the health of vulnerable ecosystems. Sulfate and nitrate as ammonium salts are also an issue, since both perturb biogeochemical cycling and ammonium becomes bio-available as an acidifier in the soil medium. The effects of acidic deposition include changes in the chemistry and biology of low alkalinity lakes and streams, as well as apparent damage to red spruce in mountainous areas of the eastern United States (e.g, Irving 1991). Nitrate deposition on watersheds, including estuaries in the eastern parts of the United States, has also been found to affect water quality through eutrophication.

The ubiquitous presence of sulfate and nitrate deposition, led to major investigations to define the nature and extent of regional pollution across North America (e.g., Hidy 1994). While regional-scale ambient PM sulfate concentrations did not appear to be of environmental concern *per se*, the nature and extent of sulfate (and nitrate) deposition and their ecological consequences were studied extensively in Canada and the United States (e.g., Irving 1991; CWS 2008). As a result of these studies and their interpretation, a major effort was undertaken to reduce regional scale sulfate and nitrate pollution in North America. The sources of concern included emissions from fossil fuel power plants in the eastern United States and emissions from major metal processing and electricity generation sources in southeastern Canada. Through implementation of Title IV of the 1990 CAAA and similar Canadian policies, annual sulfur dioxide emissions were required to be reduced by approximately 46% from estimated 1980 emissions of about 26 million t per year

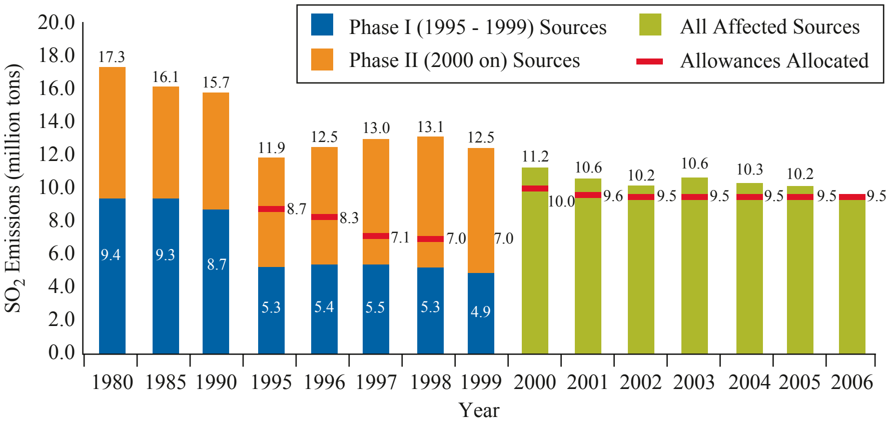

Fig. 12.9 Annual SO_2 emission declines in the Acid Rain Program Regime of the eastern United States. Cap and Trade allocations are included in the bar diagrams. (Source: EPA 2007b)

(tpy). Nitrogen oxide emissions were to be reduced by about 10%, mainly in the eastern U.S. Between 1990 and 2006, estimated NO_x emissions in the East declined from 6.7 million tpy to 3.8 tpy (EPA 2007b).

Reductions in SO_2 emissions in the eastern United States achieved by the cap and trade system established under Title IV of the CAAA are shown in Fig. 12.9. Reductions during phases I and II of the cap and trade program are shown in the diagram along with the cap and trade allocations. The annual reductions in SO_2 emissions from power plants achieved by this program in the greater eastern United States ranged from an initial high of 17.3 million tpy in 1980 to 9.4 million tpy in 2006. These emission reductions are reflected qualitatively in subsequent reductions in ambient SO_2 concentrations (Table 12.2) and in particulate sulfate concentrations (Fig. 12.8).

Independent of the U.S. initiatives, Canada also took steps in the 1980s to reduce its domestic SO_2 and NO_x emissions by reducing emissions from large point and transportation-related sources. Consequently, Canadian SO_2 emissions in 2006 were 35% less than those in 1990 and more than 55% less than the 1980 emissions. Progress towards reaching the emission-reduction goals was determined by tracking specific actions taken by the main emitters (base metal smelters), through assessment of reported emissions inventories, and by monitoring the changes in ambient concentrations and wet deposition amounts. Subsequent to these original SO_2 emission reductions, which were intended to reduce sulfate deposition below a target load of 20 kg/(ha/year), Canada adopted critical loads as its deposition standard (e.g., EC 2005). Thus, the Canadian and U.S. management strategies are fundamentally different. In the United States, the focus was on mandating reductions in emissions and verifying these reductions by measuring stack emissions from major point sources. In Canada, the approach was to rely on commitments to reduce emissions and to verify these reductions by measuring deposition loads in vulnerable areas. Although

Canadian investigators have found that levels of acid deposition have decreased in eastern Canada over the last twenty years (due to reductions in emissions in both the United States and Canada), several regions continue to receive levels of deposition in excess of the calculated critical loads (e.g., EC 2005). Evidence of the success of both these programs is discussed in the following sections.

12.4.2 Trends in Acidic Deposition and Emission Reduction

Trends in sulfate and nitrate deposition have been documented in the United States and Canada (EC 2005; CWS 2008; EPA 2007b). The U.S. observations indicate that both acidic species have declined as emissions have been reduced across eastern North America since 1980. The changes in U.S. deposition and air concentrations are shown in Table 12.6 by region. The reductions in ambient SO_2 concentrations are similar to estimated emission reductions across the eastern United States. However, the fractional reduction in sulfate in precipitation is somewhat less than the

Table 12.6 Regional changes in annual deposition of sulfate and inorganic nitrogen 1989–1991 vs. 2004–2006 paralleling U.S. emission reduction from the acid rain program. (Source: Based on CASTNET and NADP data (EPA 2007b))

Measurement	Region	Average 1989–1991	Average 2004–2006	Percent change
Ambient SO_2 (μg/m^3)	Mid-Atlantic	12.2	7.5	−39
	Midwest	10.0	5.1	−49
	Northeast	6.7	2.8	−58
	Southeast	5.2	3.3	−37
Wet sulfate concentration (mg/l)	Mid-Atlantic	2.3	1.6	−31
	Midwest	2.2	1.5	−33
	Northeast	1.9	1.1	−40
	Southeast	1.3	1.1	−18
Wet sulfate deposition (kg/ha)	Mid-Atlantic	26.8	19.2	−28
	Midwest	22.3	14.9	−33
	Northeast	22.2	14.5	−35
	Southeast	18.1	14.3	−21[a]
Wet nitrate concentration (mg/l)	Mid-Atlantic	1.5	1.0	−30
	Midwest	1.5	1.2	−17
	Northeast	1.4	0.8	−38
	Southeast	0.8	0.7	−10
Wet inorganic nitrogen deposition (kg/ha)	Mid-Atlantic	5.9	5.0	−16[a]
	Midwest	5.9	5.4	−9[a]
	Northeast	5.4	4.1	−25[a]
	Southeast	4.3	4.1	−5[a]

[a] Percent change is estimated from raw measurement data, not rounded; refined techniques for measuring and calculating percentages yield values that are at or below the sensitivity of the method may not be significant due to the combination of error and signal averaging

fractional reduction in SO_2 emissions. The influence of reductions in NO_x emissions on nitrate in precipitation appears to be strongest in the Northeast, compared with other regions, but less than the apparent reductions in NO_x emissions from sources affected by the U.S. acid rain reduction program.

In the 2004 Canadian Acid Deposition Assessment, wet sulfate and wet nitrate deposition from both the U.S. and Canadian networks were combined and integrated across all of eastern North America (EC 2005). Comparing two five-year periods, 1990–1994 and 1996–2000, the assessment found that integrated wet sulfate deposition had decreased by 16%. This finding was consistent with, but slightly less than, the integrated SO_2 emission decrease of 21% for the same area and time periods. For the same two periods, however, there were no decreases in integrated NO_x emissions or nitrate deposition. Retrospective comparisons of the original model-projected sulfate deposition reductions with the observed deposition changes showed that the regional model projections were reasonably accurate (Irving 1991). This analysis represents one of the few times that original model-derived expectations have been verified after the fact.

Dry deposition also makes significant contributions to the flux of sulfur and nitrogen species to terrestrial and aquatic ecosystems. However, dry deposition is difficult to measure directly. The CASTNET and CAPMoN networks estimate this component of the total deposition load using a model that assumes the dry deposition flux is a function of a dry deposition velocity and air concentration measurements at the site. This enables an estimate of the total deposition (dry and wet). In the eastern United States and Canada, these estimates suggest that dry deposition of sulfate and nitrate is about equal to wet deposition (e.g., Irving 1991). However, these relative contributions vary with location and also vary with the number of nitrogen species included in the estimates.

12.4.3 Surface Water Response

Table 12.7 compares changes in surface-water chemistry with estimated changes in the ambient concentrations of SO_2 and wet deposition. This comparison is an important accountability test. In the Northeast, reductions in ambient SO_2 and wet deposition of sulfate have been reflected in reductions in surface-water sulfate concentrations. These changes are particularly well documented for the lakes and streams in the Adirondack and Catskill Mountains (e.g. Burns et al. 2005). Between 1992–2001 sulfate concentrations declined in surveyed lakes in the Adirondacks by an average of 3.3 μeq/l and in surveyed streams in the Catskills by 2.5 μeq/l, which result in sulfate concentrations ≤ 20 μeq $SO_4^{=}$/l. Nitrate also decreased in concentration, but these changes were three- to ten-times less than those for sulfate. Nitrate changes are generally not consistent across the region because of variations in the biogeochemical N cycle that are driven by land use history, climate variability, and disturbances involving soil freezing, winds, ice storms, flooding, insects, pathogens, and aquatic processes.

Table 12.7 Measurements of lake water chemistry in the Adirondack Mountains. Number of lakes (out of 48) indicating significant trends ($p < 0.1$). Quantities are $SO_4^=$, NO_3^-, sum of base cation (C_B), acid neutralizing capacity (ANC), pH, inorganic monomeric aluminum (Al_{im}) and dissolved organic carbon (DOC). Average rates of change for sulfate, nitrate, C_B, and ANC are µeq/l-year. Average rate of change for Al_{im} and DOC are µmol/l-year and µmol/l-year of carbon. Changes for pH are Δ (pH)/year. (Source: http://www.nyserda.org/Programs/Environment/EMEP/project/4915/4915_project_update.pdf)

Average rates of change							
Measurement period	$SO_4^=$ decrease	NO_3^- decrease	C_B decrease	ANC increase	pH increase	AL_{im} decrease	DOC increase
1992–2000	44	15	26	29	18	28	7
	−2.57	−1.03	−3.33	1.60	0.04	−0.31	15.7
1992–2004	47	22	24	37	29	40	12
	−2.11	−0.50	−1.62	1.13	0.02	−0.16	9.6

Table 12.7 provides additional information on changes in water chemistry for a number of acid-sensitive lakes in the Adirondacks. Trends in a number of ecologically significant chemical properties were measured over two time periods, 1992–2000 and 1992–2004 in 48 lakes as part of the Adirondack Long Term Monitoring (ATLM) program (Driscoll et al. 2003, 2007a). Sixteen lakes in this data set have monitoring records beginning in 1982. The integers in Table 12.7 are the number of lakes out of 48 showing a significant trend (decrease or increase) for the quantity indicated, while the smaller decimal numbers are the average rates of change for that number of lakes. For example, 44 lakes showed significant declines in sulfate concentration for the period 1992–2000, and an additional 3 lakes showed significant declines when the measurement period was extended to 2004.

Less than half the number of lakes showed significant declines in NO_3^- concentration, consistent with the pattern for surface waters in eastern North America indicating greater improvements in sulfate response than nitrate. This difference is probably related to differences in deposition input. Unlike sulfate, which has decreased, nitrate deposition to the Adirondacks has remained fairly constant over the past 20 years (private communication, K. M. Roy, New York State Department of Environmental Conservation). Changes in aquatic nitrate concentration appear to be related not only to atmospheric deposition, but also to biological assimilation processes in terrestrial ecosystems, as noted from red maple studies combined with modeling (Driscoll et al. 2006).

Acid neutralizing capacity (ANC) showed improvement in 29 of the 48 lakes surveyed in the Adirondacks, but the change was small and slow. At current acid deposition rates, recovery to a value of ~50 µeq/l, a level believed to be suitable for the health of aquatic biota, is expected to be slow. Levels of pH increased in 18 lakes but declined in two. Overall averages in this time period reflected conditions still critical to aquatic biota with 323 lakes having $pH \leq 5.5$. Base cations and ANC show mixed response to reductions in sulfate and nitrate. Toxic forms of aluminum declined in 28 lakes, but toxic levels remained high enough to be toxic to juvenile forms of native fish (Burns et al. 2005; Driscoll et al. 2007a). The response depends on the nature of the lakes and the watersheds in relation to leaching of soils (e.g., Burns et al. 2005; Driscoll et al. 2007a).

An overview of the changes in the acidity of selected waters in acid-sensitive areas is illustrated in Fig. 12.10. The 1990–2000 comparisons suggest reductions in acidity in the upper Midwest, the Adirondacks, and northern Appalachian Plateau,

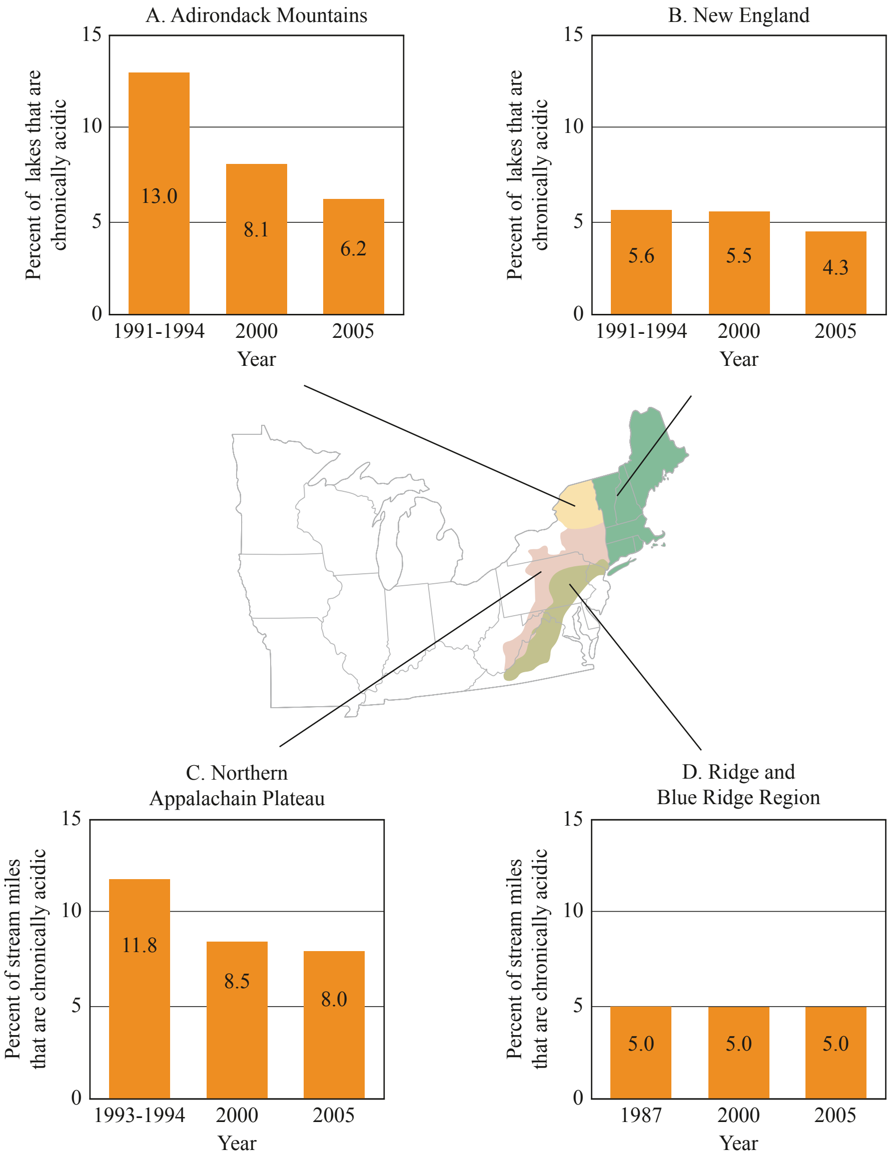

Fig. 12.10 Lake and stream acidity trends in selected acid-sensitive regions of the eastern and central United States, 1990–2000. (From EPA 2007b)

but essentially no change in the Blue Ridge Mountains or in New England. Reductions in acidity are associated with reductions in sulfate and nitrate deposition in some locations, but not in others. For example, in three different areas of eastern Canada, trends from 1988–1997 suggests that about 70% of the lakes have shown no significant change in acidity status while 25–30% showed significant improvements, and a few lakes have increased in acidity (CWS (2008)). Burns et al. (2005) indicate that even though lakes and streams are recovering from reduced levels of acid deposition, the rate of recovery is slow, based on the observations and watershed modeling: "…A quantitative understanding of the factors other than acid precipitation that may affect surface-water pH and acid-neutralizing capability (ANC) is necessary to separate the effects of the U.S. clean air laws and atmospheric deposition from natural variability and disturbances." (Burns et al. 2005)

Irving (1991) reported some consistency in selected lakes between changes in sulfate water chemistry predicted by models and observations. In terms of accountability this would be an expected consequence of ongoing and future emissions reductions. Such consistency gives decision-makers confidence in the multi-media chemistry models applicable to the eastern aquatic systems, in spite of the complexity in watershed characteristics. However, similar consistency has not been demonstrated for nitrogen compounds, probably due to the complexities of the nitrogen cycle and poor knowledge of specific soil and watershed characteristics in affected areas. Historically smaller NO_x emission reductions, compared to SO_2, have also made it harder to detect trends in lake and stream chemistry. In recent years, reductions in NO_x emissions have been larger. This larger signal may lead to detectable changes in lake and stream conditions, assuming our knowledge of the nitrogen cycle is correct.

Accounting for changes in acidity can be more complex than changes in aqueous sulfate and nitrate since the complete characterization of acidity depends on the presence of ammonium and the acid-base chemistry in watersheds and deposition. Projecting changes in surface water acidity is complicated because watersheds are "individualistic" in their acid-base chemistry. Thus, projections of changes in acidity have not materialized in the past because earlier models could not reliably account for an anion–cation balance in deposition due to inadequate cation modeling.

12.4.4 Ecosystem Response

Biologists maintain surveillance on a number of lakes in eastern Canada and the United States, and continue to watch trends in soil and vegetation conditions in several locations. This surveillance has shown that the response of aquatic and terrestrial biota to reductions in sulfate and nitrate deposition has been slow, except, perhaps, in lakes in the Sudbury, Ontario area. The Canadian Wildlife Service maintains a surveillance program for water birds and aquatic food chain monitoring (CWS 2008). These results also suggest a slow response to changes in water chemistry. This is evidently related to the limited changes in ANC and other cumulative measures of water chemistry, which have responded, but not sufficiently to be reflected in the biological indicators. Another recent assessment of biological response includes a survey of lakes in the Catskill Mountains covering the period 1987–2003. In this study, Burns et al. (2006) found no clearcut evidence of improvement in macro-invertebrates (e.g., periphytic diatoms) and certain fish species (e.g., slimy sculpin and brook trout) despite the change in acidity from reduced atmospheric deposition.

Forest response to reductions in acid deposition has been tracked in eastern Canada, with special attention to the red maple. In Quebec, the monitoring focused on tree growth and found that the hardwood and coniferous stands have experienced about a 30% reduction in growth in areas where the deposition exceeds the critical load estimates (EC 2005). Surveillance reported by Burns et al. (2006) suggests that although the rate of soil acidification has slowed, further reductions an acid deposition will be needed to achieve critical load levels in upland forest areas.

Forest conditions in the United States are monitored in experimental forests including Hubbard Brook and Walker Branch, as well as at high elevation sites in Vermont and in the Shenandoah National Park in Virginia. Surveillance of the forest conditions at these locations indicates reduced leaching of base cations as acid deposition has fallen, but to date, forest response as indicated by growth or senescence, is ambiguous, and confounded by ozone stress, climatic shifts and disease (see also Chap. 6).

12.4.5 Lessons Learned

- *To what extent have the current air quality plans followed a multipollutant framework for protecting ecosystems?*

  Initial actions taken to reduce acidic deposition focused on sulfur oxides, and only later considered the problems associated with emissions of NO_x and other nitrogen species. Since that time, ecosystem research has shed considerable light on watershed chemistry and the associated mechanisms of damage, as well as on the effects of deposition of ammonium and heavy metals, especially mercury. In spite of the recognition that the effects of air pollution on ecosystems, both aquatic and terrestrial, are inherently multipollutant in nature, there is no example of a comprehensive multipollutant air quality management action being taken to protect ecosystem health other than the mandated reductions of sulfur and nitrogen oxides.

  The multipollutant nature of acidic deposition involves complex interactions between pollutants and atmospheric processes, and physicochemical interactions with other media and biota on a scale largely unknown prior to the 1980s. Sulfate and nitrate are the important acidity anions, but acidification (and consequent Al release) is likely to be most important for the health of vulnerable ecosystems. Effects of acidic deposition on vegetation are complicated by damage from ozone exposure, and the interactions of various metals either by direct deposition, or by exchange through soil and water media. While pollution management remains focused on impacts on humans as the highest priority, the issues of ecosystem stress have become an important adjunct in remote areas where vulnerable systems exist.

- *In the light of knowledge about emission changes, does the available information provide confidence in the ability to assess the effectiveness of the management strategies adopted to reduce concentrations of each of pollutant or pollutant group?*
  Deposition measurements and aquatic chemistry networks in the United States and Canada demonstrate that actions taken to reduce emissions of SO_2 have been effective in reducing acidic deposition and sulfate concentrations in surface waters. There is less evidence that reductions in NO_x emissions have been as effective. It is also clear that changes in integrated measures of surface water quality, such as ANC, have been slower than expected. Thus, progress toward recovery of aquatic systems could be a lengthy process.
  Measurement of change in acid deposition has relied on sulfate and nitrate constituents as indicators of the effects of acidic deposition on the chemistry of vulnerable surface waters and terrestrial systems. The changes seen in these two chemical indicators, as observed by monitoring networks in Canada and the U.S., provide strong evidence of reduction in acid deposition in the eastern half of the continent. However, their measures of potential ecosystem benefits are incomplete without the corresponding changes in base cation deposition, and the soil/watershed base cation availability. The presence of ammonium/ammonia in precipitation or in dry deposition complicates acidification of ecosystems. Ammonium is distinct from other base cation species in that the nitrogen associated with this species acts as an acidifier in the soil-biota medium quite distinct from strong acids of sulfur and nitrate. Trends in the wet deposition of this form of nitrogen are well-tracked by the monitoring.
- *Does the knowledge about environmental effects give confidence in the ability to assess whether changes in regulated pollutant indicators will result in improved ecosystem health in North America?*
  Although there is clear evidence that actions taken to reduce acid deposition have been effective, especially for sulfur compounds, it is less clear that these actions have been sufficient to ensure recovery of affected ecosystems, both aquatic and terrestrial. The recovery response of these systems has been slower than expected, and a longer monitoring record may be needed before the answer to this question is clear. This lack of knowledge is partially due to the lack of long-term monitoring of these systems.
  Measured changes in sulfate and nitrate deposition to vulnerable ecosystems combined with changes in water chemistry provide confidence in the ability to assess the effectiveness of management actions for reducing ecosystem exposure to acid deposition. However, the indicator changes fall short of providing a complete picture of biological response either in water, soil media or vegetation. The correspondence between SO_2 and wet sulfate deposition has influenced water chemistry, as projected by combined deposition and watershed chemistry

models. To date, the changes in nitrate with NO_x emission changes are not well established. Due to the time scales required for recovery and the complexity of the aquatic and terrestrial ecosystems, many years may pass before the response of the biological component, as measured by changes in key biological indicators, may be found (see also Chap. 6).

Critical and target loads are practical measures of ecological risk for aqueous and terrestrial systems. These concepts are probably better supported for surface water impact than for terrestrial ecosystems, which are more complex in their response with interactions between both soils and vegetation.

- *To what extent were multipollutant effects recognized and deficiencies accounted for in the evolution of management practice?*

  In early deliberations about acid deposition, acidity was mainly associated with the sulfate anion. With research that began in the 1980s, scientists developed knowledge about the importance of nitrate, and ammonium in ecosystem chemistry. However, interest in developing a "standard" for acid deposition in terms of a critical load focused mainly on wet sulfate deposition as a surrogate for acidification. The critical load concept has been adopted by Canada for ecosystem protection, but it has not been adopted as a standard in the United States or Mexico. Modeling projections for sulfate and nitrate deposition has been a key element in the design of U.S. and Canadian strategies along with monitoring of regional air concentrations, deposition rates, and water chemistry in order to demonstrate the effectiveness (i.e., accountability) of these strategies. The Title IV provisions of the U.S. CAAA included reductions in region-wide emissions of SO_2 and NO_x across the eastern United States in order to address acid deposition. In Canada, the critical load target is the means for achieving aquatic and terrestrial ecosystem management. These approaches focus on the acidification anions, and to a much lesser extent the complete acid-base chemistry involved in "vulnerable" aqueous and terrestrial ecosystems.

  Ecologically based "standards" for hydrogen ion and nitrate remain less well-developed than for sulfate. Recent work has also focused on critical and target loads for both hydrogen ion and nitrate. Progress in defining these goals would enhance the multipollutant options for management practices

12.5 Hazardous Air Pollutants

The regulatory approaches for air toxics differ substantially from the management of criteria pollutants. In Mexico virtually no strategies exist for the reduction of air toxics (Table C, p. xxvii). Canada has a national listing of these chemicals (Table B, p. xxvi), which is smaller in number than the U.S., and is mixed with the U.S.-designated criteria pollutants. Although the U.S. lists 187 HAPs (Table A, p. xxiv), most of the focus on long-term measurements has addressed only a subset of these pollutants. A number of the HAPs relate to speciated VOCs, and some are products (e.g., the aldehydes) of photochemical processing. The measurements are very limited in spatial extent, principally in the U.S., but they indicate generally a reduction in the compounds of concern. However, a few have evidently increased in ambient concentrations. Applying an accountability analysis to the HAPs is complicated by the method of determining risk, which is based on a fictional "most exposed individual". After a model calculation of ambient concentrations, the maximum achievable control technology is applied to sources. While modeling is used for estimating local maximum concentrations, long-term ambient measurements are not in place. Accountability involves determining change in specific disease markers such as cancer; these population determinations have not been done, except for lead.

12.5.1 Evolution of Strategies

The definition of hazardous air pollutants differs among the three countries of North America.[8] In the United States, they are defined as the 187 air toxics listed in the Clean Air Act. This list is much broader in scope than the toxics listed in Canada. Mexico, on the other hand, informally designates a subset of HAPs. In order to get better information on the HAPs situation in Mexico, work has been recently undertaken in Mexico City to develop a HAPs emission inventory.

The U.S. air toxics listing ranges from generic material, such as coke oven emissions and asbestos fibers, to specific chemical compounds associated with petrochemical feed stocks (e.g. benzene, toluene and xylenes—BTX), and pesticides. The HAPs can be grouped in terms of common sources (e.g., Table 8.2) or in terms of reaction chemistry (e.g., Table 7.3). Human health risk from exposure to HAPs has traditionally focused on inhalation impacts, except for some persistent organic pollutants (POPs), which for present purposes also includes mercury in its methylated form. The inhalation pathway is emphasized because: (a) carcinogenic risks generally ensue at lower threshold doses than non-carcinogenic risks for the same HAP; (b) exposure doses are more easily calculated for an inhalation route than other pathways; and (c) many fewer data are generally available on exposure and dose-response through non-inhalation routes. However, for some important HAPs inhalation is not the most important exposure pathway. Mercury is among these pollutants, along with certain pesticides and certain radionucelides, such as uranium, plutonium, and neptunium.

Control of HAPs, at least in the United States (see Text Box 12.2), is addressed through emission limits and emission controls (e.g., maximum achievable control technology—MACT). The risk of exposure to single HAPs is assessed by estimating risks to individuals or to populations (see also Chap. 3). This is done either by modeling using measured or estimated emission concentrations, or by comparing measured ambient concentrations to risk-based limits. Monitoring of HAPs is generally more limited and sporadic than the monitoring of CPs; in addition, there are fewer regulatory limits on ambient HAP concentrations compared with the CPs.

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[8] Regulated pollutants for Canada, the United States, and Mexico are defined in the List of Terms.

Because of these limitations, current monitoring provides only a partial picture of HAP concentration patterns.

Text Box 12.2 Treatment of Hazardous Air Pollutant in the U.S. Regulations

The 1970 U.S. Clean Air Act (CAA) defined two principal types of air pollutants for regulation: CPs and HAPs. The CAA at the time required the EPA to identify all pollutants not classified as CPs as those that "…may be reasonably anticipated to result in an increase in mortality or an increase in serious irreversible or incapacitating reversible illness…" EPA was required to establish NAAQS for the CPs for which air quality criteria had been issued. The CPs were addressed as a single pollutant air quality management program that required a national approach. This philosophy was based on the premise that the federal government should deal with issues that were national in scope, or where air pollution crossed political boundaries, and that state and local governments should deal with more localized issues. In 1970, the first eight pollutants were identified as HAPs; they included asbestos, benzene, beryllium, inorganic arsenic, mercury, radionuclides, and vinyl chloride. This definition was later expanded.

The process for regulation of HAPs was described in the 1970 Clean Air Act Amendments (Sect. 112) in general terms only. EPA was to list substances that met the definition and publish national emission standards for HAPs (NESHAPs) providing, "…an ample margin of safety to protect the public health from such hazardous air pollutant[s]." The use of the term "ample margin of safety" for hazardous air pollutants, as opposed to "adequate margin of safety" for CPs, implied more stringent control, although the distinction was not clarified. Sect. 112 relied largely on EPA to develop and carry out the hazardous air pollutant control program although it provided for the delegation of enforcement authority to state and local agencies.

In 1977, the CAA was revised, including the hazardous air pollutant provisions. One change incorporated in 1977 expanded the definition of emission standard to include design, equipment, work practice, and operational standards. Through a series of administrative and court actions in the 1980s, EPA was allowed to consider costs and risk-benefits as part of the control of HAPs.

The subsequent 1990 CAAA fundamentally restructured Sect. 112 to establish an aggressive new program for the regulation of air toxics. Specific programs were established for the control of major source and area source emissions, including the electric utilities, refineries and chemical plants, the control of non-biodegradable compounds, the protection of the Great Lakes and coastal waters, the regulation of emissions from incinerators of all types, and the control of chemical accidents.

The 1990 CAAA established a statutory list of 189 (later reduced to 187) substances that are formally designated as HAPs, thereby short-circuiting the listing process that proved to be a major obstacle to regulatory action in prior years. EPA then produced the current list of categories of major sources and area sources of each listed pollutant, promulgated standards requiring installation of the maximum achievable control technology (MACT) at all new and existing major sources in accordance with a statutory schedule, and established standards to protect the public health with an ample margin of safety from any residual risks remaining after application of MACT technology.

Regular measurements of HAPs are made within the PM_x composition networks, which provide measurements of metals, and the photochemical assessment measurements networks PAMS, NAMS/SLAMS and NAPS (Canada). These latter networks provide measurement of VOCs such as benzene, the xylenes, toluene, and 1, 3-butadiene. More extensive measurement programs have been carried out (e.g., the urban air toxics monitoring program, or UATMP), but these programs are limited in terms of temporal and spatial coverage. Mercury, specifically divalent mercury, has been measured at a number of locations by the U.S. Mercury Deposition Network (MDN) of the National Atmospheric Deposition program and by the Canadian (CAMNet) network (see also Chap. 10). Even in these networks, field-capable methods have limited mercury measurements to wet deposition collection at the monitoring stations and gaseous elemental mercury at some locations. No sustained nationwide trends have been established, but some regional patterns have emerged from these data (Butler et al. 2008).

The U.S. approach to controlling HAPs has focused on primary emissions; however, some HAPs participate in or are formed by the photochemical cycle. These reactive HAPs include the aldehydes, 1, 3-butadiene, acrolein, and the aromatics, especially benzene, styrene, toluene, and xylenes. As discussed in Chap. 7, the reactive HAPs yield a complex array of trace chemical products, most of which have not been identified, or investigated, as toxic agents. Risk of exposure to HAPs formed through secondary reactions in the atmosphere has not been considered in traditional air quality management. However, they might be considered as part of a multipollutant air quality management approach. For management purposes, these HAPs will probably require grouping either by source (Chap. 8) or in terms of their chemistry (Chap. 7).

12.5.2 Trends in HAPs and Emission Reductions

Emissions inventories for 33 priority HAPs (32 listed HAPs plus diesel particulate matter) have been prepared under the terms of the National Air Toxics Assessment (EPA 2002c), and separately under the Toxics Release Inventory (which is based on multimedia source reporting). Little direct evidence of emission trends is available from inventory tracking. However, it is assumed that many emissions have declined since the 1990s due to imposition of MACT on a number of sources (e.g., VOCs from refineries and chemical plants, and mercury from municipal waste incinerators).

A representative survey of HAPs concentrations across the United States is contained in the NATA (EPA 2002c) based on intermittent sampling from 1988 through 2000. Recently, McCarthy et al. (2007) reviewed some of these measurements and analyzed available data for a number of HAPs using emission reports from across the United States for the period 1990–2003. The observations were limited in terms of location, duration, and quality; but nevertheless provided insight on the post-1990 trends for 15 of the 187 designated species. Estimated concentration trends for these selected HAPs are shown in Fig. 12.11a, b. The results indicate that concentrations of organic compounds from o-xylene to tetrachloroethylene (TCE) have declined during the past decade or so as have the metals, Pb, Cd, and Mn. Chlorinated compounds show decreasing chloroform concentrations, but trichloroethylene to methylene chloride have not changed.

In addition to these general trends, Fig. 12.11a, b shows that acetaldehyde, a photochemically related compound, has changed little, while formaldehyde concentrations apparently have risen. Chromium and arsenic also appear to have increased in concentration. Although the authors did not provide specific data on emission trends, they speculate that the trends found in the observations are related to emission changes during the 1990s.

Another example of HAP tracking comes from New York State. Aleksic et al. (2005) report changes in benzene concentrations in rural and urban areas of New York State from 1990–2003. Their analysis of ambient data indicates that benzene concentrations have declined both in urban and rural areas over this time period. Since the decline occurs in both cities and rural areas, one concludes that the change is likely related to modifications in gasoline blends across the region.

A third example of HAPs tracking comes from monitoring activities in the Los Angeles area (SCAQMD 2000, 2008). Measurements of 30 HAPs have been recorded in the Los Angeles area since 1990, including organic species, carbonyls, toxic metals, and PAHs. From 1990 to 1997, the monitoring indicates that overall, concentrations of these carcinogens have declined.

A fourth example is a major program to survey a number of HAPs in the Great Lakes region (Sun et al. 2003). This monitoring study covered several years, which covered both urban and rural sites surrounding the Great Lakes and included a range of toxic pollutants from the light VOC fraction through several pesticides. The trends reported suggest a general pattern of decline across the region, presumably as a result of state and local control programs as well as federal attention.

The HAPs listings were prepared based on carcinogenic potency and reproductive (teratological) risks. Other than toxicological research to establish some estimate of dose-response and exposure estimation from ambient data, no systematic investment in ambient measurements has been made to track these compounds or elements, except, perhaps, for certain pesticides or POPs. Thus at this time, there appears to be little knowledge about the relation between changes in emissions of HAPs and exposure, or changes in local or national risks associated with their presence in the ambient air. A possible exception might be a unique risk assessment of

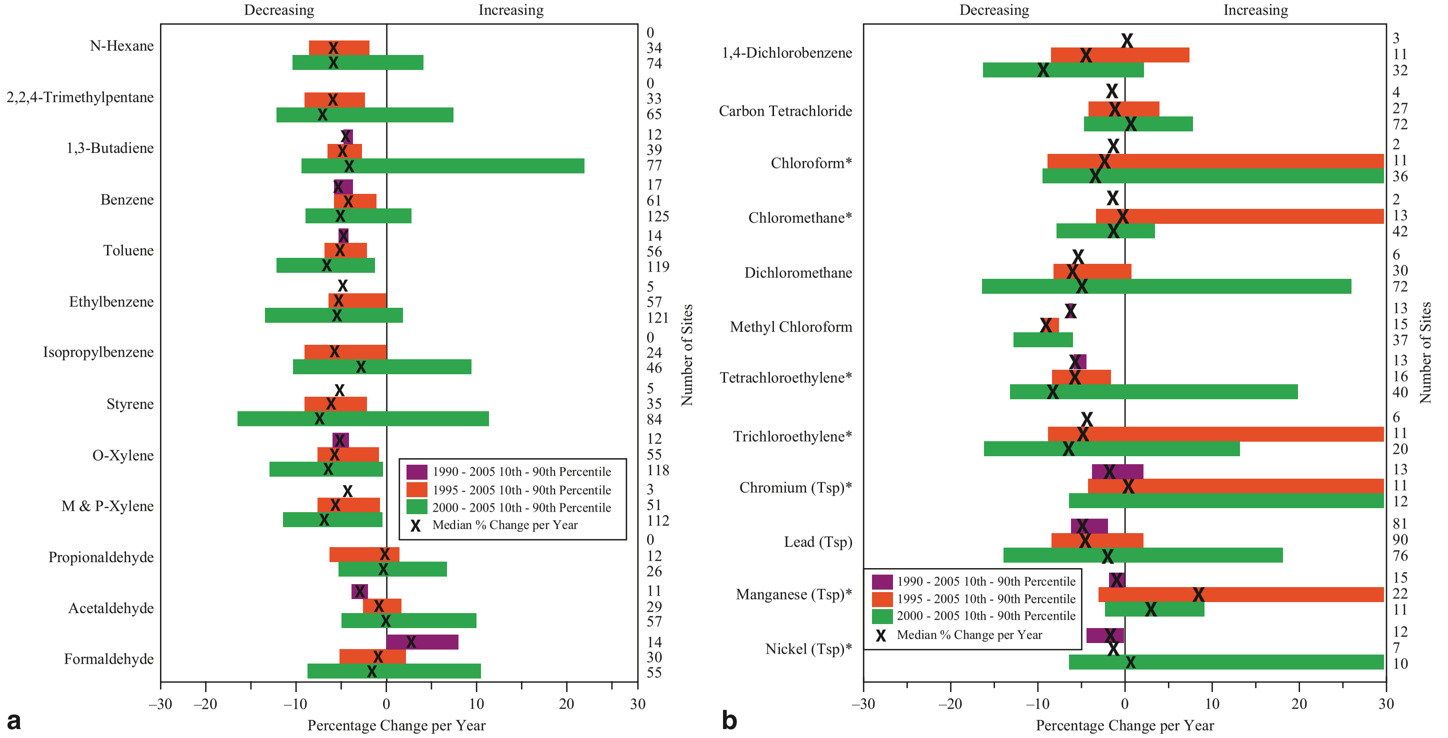

Fig. 12.11 Trends in HAPs concentrations of various organic compounds (**a**) and of various chlorinated organics and metals (**b**) in the United States based on ambient air monitoring data between 1990 and 2003. (From McCarthy et al. 2007)

HAPs, including an estimate of population carcinogenic risk based on monitoring and modeling, conducted by the SCAQMD (2000, 2008). The study used available data from federal sources and the State of California to estimate a population risk that exceeded a cancer incidence of about 1400 per million people. The study concluded the greatest risks were from mobile source emissions, with the largest contribution being diesel engine emissions.[9]

Results of a first step towards including both criteria pollutants (ozone and $PM_{2.5}$) and a subset of HAPs in air quality (CMAQ) modeling was reported recently by Lueken and Cimorelli (2008). The modeling was conducted for a Philadelphia case study covering the months of January and July 2001. The calculations evaluated the impact of reductions in NO_x on ozone, and nitrate ($PM_{2.5}$) as well as on formaldehyde, acetaldehyde, acrolein and benzene. The calculations suggest that NO_x reductions expected from CAAA initiatives should reduce ozone and $PM_{2.5}$ as well as concentrations of formaldehyde in the Philadelphia domain, but they should slightly increase the concentrations of the other species, except benzene. These calculations provide an early exploration of co-dependencies of CPs and HAPs for purposes of optimizing management strategies.

12.5.3 Health and Ecological Effects of HAPs

The human health response to HAPs exposure includes carcinogenic effects and other impacts, such as reproductive effects. The HAPs included in the CAAA list have been subjected to toxicological screening for their mutagenicity or carcinogenicity, or other physiological stresses. Dose (concentration)-response levels exist for some of them, but in general there is relatively little information on absolute risk or on thresholds for significant risk. Risk assessment for HAPs is based on maximum exposed individuals, with a residual risk, after application of MACT, considered arbitrarily to be one chance in a million for premature death.

At the present time, there is relatively little epidemiological knowledge about the consequences of pollution exposure to HAPs, though obviously some information exists for lead, mercury and arsenic, as well as asbestos and PAHs. The risks of exposure rely heavily on toxicological studies in the literature as the primary basis for guidance on exposure-health response relationships (e.g., HEI 2007).

Recently, Wang et al. (2009) have reported investigation of personal exposure to HAPs using data from the NHANES study that accounted for socio-economic, demographic and behavioral variables. Their work covered three chlorinated compounds and the BTX group and indicates potentially important variations in exposure by activity, residence, and work/school environments. The study also included a statistical inference of significant factors affecting exposure.

Although ecological effects do not typically drive risk assessments for HAPs, EPA is required to consider such effects under the CAA, Sect. 112.

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[9] Diesel engine emission are currently not listed a HAP under the CAA.

12.5.4 Lessons Learned

- *To what extent have the current air quality plans followed a multipollutant framework for HAPs?*
  Reliance on emission standards for the HAPs has simplified issues of HAPs management and consideration of multipollutant interactions. However, the emission-standards approach has largely disregarded the chemical reactivity of these pollutants in the atmosphere, and it has circumvented considerations of controlling sources that are also sources CPs. There is relatively little information reported on potential chemical interactions among the HAPs. These substances are governed by a single-pollutant air quality management strategy, and their reactivity is generally not incorporated in dispersion modeling or ambient observations.
- *In the light of knowledge about emission changes, do the available tools provide confidence in the ability to assess the effectiveness of the management strategies adopted to reduce concentrations of each of pollutant or pollutant group?*
  Sustained measurements of HAPs are fragmented spatially and temporally, making nationwide accountability for reductions and risk management problematic. However, reported studies of trends in certain locations offer encouraging evidence that ambient concentrations of HAPs have been reduced by implementation of MACT in the United States. In Canada, systematic measurements of air toxics includes metals in particulate samples and speciated VOCs at subset of NAPS sites across the country. Aldehydes are also measured routinely, but at a smaller subset of these sites. Consideration of air toxics in Mexico has only just begun. The first step has been a recently completed inventory of selected HAPs in Mexico City. Within Mexico City, some data exist for speciated VOCs, including some HAPs, but little has been done to this date on identifying sources and source emissions in other locations.
- *Does the knowledge about environmental effects give confidence in the ability to assess whether changes in regulated pollutant indicators will result in improved public health and ecosystem health in North America?*
  The methods for assessing the health impact of air toxics are different from those used for evaluating the risks of exposure to CPs. Integration of the CP and HAPs approaches for multipollutant air quality management would require a means for treating these pollutants uniformly in terms of air quality goals and health effects. The surveys of HAPs concentration trends in the United States suggest that reductions in human exposure have occurred. However, the limited results available provide a low level of confidence in our ability to assess whether or not general population health has improved with these reductions.
- *To what extent were multipollutant effects recognized and deficiencies accounted for in the evolution of management practice?*
  The listed HAPs do not recognize multipollutant interactions; indeed they are based mainly on the laboratory-based toxicity of individual species. In addition, HAPs are not discussed in terms of post-emission toxic end products that could

be produced as a result of atmospheric processing. There is some knowledge of their atmospheric chemistry for gasoline or fuel related species, but in many other cases this chemistry is unknown.

In terms of management, HAPs are addressed, by law (especially in the U.S.), according to specific sources or industries and exposure is only considered crucial near these sources. Follow-up on the effectiveness of emissions reductions is generally conducted through audits or source testing. Trends in ambient concentrations have been investigated for only a subset of HAPs and for only a few locations.

12.6 Mercury-A Multimedia Toxin

Regulatory authorities developed a strong interest in mercury as a HAP after 1980. This metal is unique in its toxicity in that methyl mercury, specifically, is the most toxic form of this metal species. The mercury exposure pathway to humans is dominated by the food chain, specifically through fish consumption. Mercury is a pollutant with a long atmospheric lifetime, so mercury contamination in North America comes from both local and global sources (see Chap. 11). Atmospheric mercury contamination is measured mainly in terms of wet deposition. Its presence in aquatic and terrestrial ecosystems has been observed for a number of years. Historically, deposition of mercury increased substantially during and after the industrial revolution. However in recent years, mercury deposition rates appear to have stabilized or declined in North America as a result of the reduction of major sources of the metal. Tracing human mercury exposure through fish consumption has been very limited. However, some evidence of reduction in blood mercury has been reported through the U.S. NHANES studies of pregnant women. This qualitative result is an encouraging, albeit preliminary, indication of declining trends in mercury exposure.

12.6.1 Evolution of Strategies

Of the listed HAPs, mercury is one of the species receiving major public attention in North America at this time (e.g., Chap. 5 and HBRF 2007). Over the past 270 years, there is evidence of dramatic increases in anthropogenic mercury in the environment due to deposition from global sources (Schuster et al. 2002). The metal is found in the environment in different valence states and phases, including a particulate species (HgP), mercury vapor Hg(II), metallic Hg(0), and in the highly toxic form of methyl mercury (MeHg). Because of its long residence time in the atmosphere, metallic mercury is a world-wide contaminant with a variety of sources both natural and anthropogenic. Anthropogenic sources include mining and industrial operations. Mercury compounds are also recycled between the atmosphere and the Earth's surface via soil–air exchange. Mercury in valence states other than metallic appears to have shorter residence times in the atmosphere; thus, these forms are deposited fairly close to their sources. In North America, two important mercury sources of concern are municipal incinerators and coal-fired power plants. Emissions from the latter are believed to be mainly as a metal, metal oxide, or salt (e.g., Hg(II) or HgP).

The net deposition of mercury consists of local emissions superimposed on a "large" global baseline (e.g., Seigneur et al. 2004). However, understanding the cycling of mercury through the environment is complicated by its chemistry and by its ability to pass into different phases. Mercury displays both diurnal and seasonal variability (e.g., Liu et al. 2006), and its various chemical forms are reactive in the atmosphere and in solid media. The atmospheric chemistry of mercury remains controversial, but the oxidation of gaseous mercury is driven by photochemical processes involving ozone and OH (e.g., Text Box 7.2; Calvert and Lindberg 2005; Seigneur et al. 2006). Exchange between mercury contained in natural rock or soil substrates and the atmosphere is also facilitated by reactions with ozone (e.g., Engle et al. 2005). This pathway provides a means for mobilization of mercury from the pedosphere, and it adds another source to the atmosphere.[10]

Once entering the biosphere, mercury species may be converted to MeHg, and are transferred into the food chain largely as this species. While emissions of mercury are quite small by mass compared with most pollutants, including CPs and many HAPs, this element has received considerable attention in North America because of its toxicity, its capacity for bioaccumulation, and its unique exposure pathway relative to other air pollutants. This exposure pathway results from accumulation of the methylated form, principally in aquatic species such as fish, which are then consumed as human food (see also Chap. 6). As the principal pathway of exposure for humans is through the consumption of food, significant mercury exposure appears to be limited to a relatively small population that might consume large quantities of mercury contaminated fish or other foods. This limited exposure pathway probably places mercury at a fairly low human population risk compared to the CPs and other HAPs. Nevertheless, considerable attention has been, and continues to be given to reduction of mercury in the environment. This concern is driven both by concerns for continental and global subpopulations exposed to mercury in the food they eat and for susceptible species of wildlife, which unlike humans may not be able to avoid exposure.

Current anthropogenic emissions of mercury in the United States and Canada are estimated to be about 150 tpy, with approximately 50 tpy associated with coal combustion. These emissions appear to be decreasing, and estimated emissions for North America are less than those reported a number of years ago. These decreases have taken place as a result of emission reductions due to regulatory requirements (e.g., MACT for municipal and medical waste incinerators). Additional strategies have been considered in the United States for coal-fired power plants. Although emissions within North America may be decreasing, emissions from sources outside

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[10] Mercury from soils can be natural or anthropogenic in origin. The latter consists of mercury deposited from the atmosphere in the past and stored in the soil for an unknown period of time before release.

the continent (particularly in Asia) are not. Modeling studies indicate that only 20–30% of total mercury deposition to North America comes from continental sources (see Chap. 11). Thus, except for local mercury deposition "hot spots" (defined as relatively small areas where mercury deposition or exposure significantly exceeds that of the surrounding region) most of the mercury reaching North America comes from sources outside the continent.

12.6.2 Trends in Mercury Deposition and Emissions

Trends in environmental mercury concentrations have been measured, at least qualitatively, for sometime from atmospheric deposition patterns, from sediment or soil sampling, and from fish sampling. Perhaps the longest record of mercury deposition derives from Upper Fremont Glacier (Wyoming) ice cores, an example of which is reported by Schuster et al. (2002). The record covers the period from about 1720–1993. Over the full period, anthropogenic inputs are estimated to be about 52%, volcanic events about 6% and background sources about 42%. Over the last 100 years, however, anthropogenic sources increased to about 70% of the total input. This record suggests a 20-fold increase in mercury deposition from 1840 until present, much larger than the 3- to 6-fold increase reported from sediment cores. Except for the North American Arctic, mercury deposition data suggest a decline in mercury deposition since the 1970s, which is roughly coincident with decreases in SO_2 emissions from coal-fired power plants and associated decreases in S deposition.[11]

A pattern of variation in mercury concentration over the last few years can be seen in the U.S. mercury deposition data. Lynch et al. (2001), for example, have cited the national (wet) mercury deposition network annual average data, and Butler et al. (2008) have reviewed recent regional trends in mercury wet deposition since the 1990s. These studies have suggested a stabilization of mercury levels and declines in some areas. Lindberg et al. (2007) also found that mercury concentrations over the past decades have been relatively stable. The mean values range from 9.2 to 10.7 $\mu g/(m^2/year)$ with no obvious trend over this time period. In contrast, Glass and Sorenson (1999) reported an increase of about 5%/year (average deposition of 7.4 $\mu g/(m^2/year)$) in deposition in the upper Midwest between 1990 and 1995. Sediment and glacial core data suggest that major increases in environmental mercury concentrations appeared with industrialization into the mid-twentieth century. However, with the possible exception of the U.S. Midwest in the 1990s, deposition concentrations appear to have declined in recent years with increased attention to emission controls, and constraints on the use of the element in industrial applications.

Even though wet mercury deposition is measured with the MDN, a routine network for measuring dry deposition has not been implemented. Reports of special dry deposition observations suggest that this component is about 75–80% of the total de-

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[11] Hypothetically this may be more than a coincidence with lower sulfur fuels, and application of control technologies may have had an unexpected consequence of reducing mercury emissions.

position to forest ecosystems. This fraction is substantially larger than the fraction that the dry component represents for total sulfur or nitrogen deposition. In order to obtain a complete picture of mercury deposition to North America, systematic measurements of dry deposition will need to be added to the existing wet deposition network.

Information on trends in mercury for Canada can be obtained from the CAM-Net network. For example, declines in total gaseous mercury have been reported in urban areas, mostly in Toronto and Montreal, between 1995 ands 2005 (e.g., Temme et al. 2007). Analysis of sediments for mercury and other metallic elements (including some HAPs) in the St. Lawrence Valley of Quebec (~1942–1995) indicate interesting changes in these trends over time (Gelinas et al. 2000). The Gelinas et al. results indicate a steady increase in less mobile elements, including mercury, vanadium, chromium, nickel, and cadmium between 1942 and 1975, followed by a period of stability. From 1982 to 1995 there appears to have been a slight decrease in mercury concentrations in Canada. There is no reported long-term record of mercury deposition in Mexico.

Global and local-scale mercury deposition modeling have been developed to include hte known or hypothetical chemistry (Seigneur et al. 2006). The model used by Seigneur et al. has been tested with available mercury data for simulations relevant to deposition patterns across the United States and Canada. While the modeling has been used for strategy development, considering apportionment between global and regional mercury and its species, it has not been adopted for retrospective analyses to compare with limited trend data and to establish a history of potential exposure beyond the available measurements (see Chap. 11 for more discussion of this issue).

12.6.3 Health and Ecological Effects

There is little information in the literature regarding long-term trends in human illness associated with environmental exposures to mercury. Lipfert et al. (2005) have reviewed the methodologies for mercury risk characterization, and the options for managing this risk from the point of view of public health protection. Their conclusions suggest that management options exist that may be more cost effective for protecting the public from the consequences of mercury exposure than simply reducing local air emissions.

There is little current information on mercury trends in the biosphere, although programs are in place to gather such data (e.g., Chap. 6; HBRF 2007; Schoch et al. 2007). A few studies are currently underway in the Adirondacks. These studies include monitoring mercury accumulation in the common loon (the loon, for example, can bioaccumulate as much as 10^5 times the mercury found in surface waters) and in prey fish; and tracking water chemistry and sediment properties. The loon program is in its early stages of interpretation, but it has already shown that 17% of the loons captured on about 40 lakes for the survey have mercury levels that place loons at risk for harmful effects of the metal. Interpreting trends in environmental exposure, however, will be complicated by the combined contributions of global and local sources on deposition and biotic assimilation.

Driscoll et al. (2007b) and Evers et al. (2007) describe recent investigations of hot spots for mercury bioaccumulation in wildlife in the northeastern United States and southeastern Canada. Their results suggest a range of accumulation depending on species and location, with one hot spot in the northern Massachusetts-southern New Hampshire region. Other hot spots may include the Minnesota-Wisconsin lake region, and the Southeast, particularly parts of Florida. The identification of areas of relatively high mercury concentrations in the Everglades and how these concentrations declined as local mercury emissions were reduced is of interest in understanding the hot spot issue (e.g. Atkeson et al. 2003). Emissions from local municipal incinerators were identified as a likely source of enhanced local deposition, and actions were taken to reduce these emissions.[12] This reduction was accompanied by a reduction in mercury found in predatory fish, such as large mouthed bass, and in the feathers of wading birds. These results suggest that the potential for human exposure to mercury from fresh waters in southern Florida has been reduced. Nevertheless, the actual or quantified risk of human population or individual mercury exposure from the consumption of fish taken in the affected areas remains unknown.

Detection of mercury effects on humans is very difficult to determine since the portion of the population of North America that relies on freshwater fish as a major food source is small,[13] and the health endpoints associated with mercury exposure are not generally reported by physicians. It is even difficult to determine how many mercury contaminated fish are consumed as part of human diets in various locations. Even with this caveat, recent evidence from a survey of blood mercury levels in young children and women of child-bearing age using the NHANES data base suggests a non-statistically significant decline in this measure between 1999 and 2002 (Jones et al. 2004; CDC 2005). In the mercury case, information on population exposure due to diet is emerging, but a complete risk analysis has yet to be reported in terms of documenting neurotoxic responses in human populations.

12.6.4 Lessons Learned

- *To what extent have the current air quality plans followed a multipollutant framework?*

  Mercury is a unique air pollutant in almost every way. Its risk to humans and biota comes from ingestion of food that has bioaccumulated the metal. The atmospheric concentrations of mercury are very low, and its sources have a frac-

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[12] This interpretation has been questioned in that there were changes in water quality management practices taking place at the same time, and modeling indicated that the global mercury contribution was large in the Everglades (see for example the review of Pollman et al. 2007).

[13] Global population exposure to mercury from the marine fish supply, including tuna and swordfish or other predatory species, may be large, but exposure is highly uncertain.

tionally larger global component than any other currently regulated pollutant. Mercury has three chemical states of concern, one of which, methyl mercury (MeHg), is highly toxic. MeHg is not produced in the atmosphere via photochemistry (although the mercury cycle is affected by atmospheric processes). It is produced by biochemical processes that take place in soil and wetland media. Human risk to mercury exposure is avoidable to most of the population of North American, but it could be a problem for small subpopulations relying heavily on fish as a food staple.

Mercury could be treated as a single-pollutant issue. Yet the metal has sources in common with other pollutants, particularly coal-fired electricity generation and refuse incineration. While its atmospheric chemistry is affected by photochemical oxidation, the metal plays no role in creating atmospheric end products relevant to health or ecological risks beyond its own compounds. Mercury also does not pose an inhalation risk, so there is little reason to consider it as part of a risk-based multipollutant strategy focused on reducing the risks of inhaling ambient pollutants. The principal reason to consider mercury as part of a multipollutant approach derives from the sources it shares with other ambient pollutants and the fact that actions taken to reduce emissions of other air pollutants can affect emissions of mercury. For example, the reduction of mercury emissions from coal-fired power plants can be obtained as a co-benefit from other emission control devices including SO_2 scrubbers and particulate collectors.

- *In the light of knowledge about emission changes, do the available tools provide confidence in the ability to assess the effectiveness of the management strategies adopted to reduce concentrations of each of pollutant or pollutant group?*

  Trends in mercury deposition since the beginning of the Industrial Revolution have been reasonably well documented in terms of deposition to the earth's surface or changes in water chemistry. However, recent short-term trends in North America resulting from changes in local and global sources are more difficult to determine since deposition measurements have only been in place for a few years. Further, a widespread dry deposition network has not been implemented, leaving a large portion of total deposition poorly characterized. The data that are available yield mixed results in terms of these short-term trends.
- *Does the knowledge about environmental effects give confidence in the ability to assess whether changes in regulated pollutant indicators will result in improved public health and ecosystem health in North America?*

  The scientific understanding of the mercury cycle gives some confidence that we can assess how changes in mercury emissions would improve ecosystem conditions. And in fact, the risk to ecosystems could be a driving force for mercury regulation. However, our knowledge is incomplete for assessing how such changes would affect general pubic health. Programs currently underway to track affected bird and fish populations in the Adirondack Mountains, Florida, and in eastern Canada will provide information on those locations, but these activities will require several years to come to fruition. The NHANES blood mercury program provides a first attempt to assess changes in human exposure in analogy to the blood lead surveillance program. However, a plan has not yet been developed for prospective studies of affected populations in terms of neurotoxic effects or changes.

Mercury effects associated with its exposure to humans and other biota could be further examined for priority of consideration in a relative risk framework. The discussion by Lipfert et al. (2005) provides a basis for conducting analyses of the relative risk of exposure to MeHg. Conceptually, this approach could be followed as part of a multipollutant air quality management approach to determining how the risk of mercury exposure ranks in comparison to the risks estimated for other HAPs and CPs.

- *To what extent were multipollutant effects recognized and deficiencies accounted for in the evolution of management practice?*

  When the issue of mercury as a bioaccumulator was initially addressed in the 1980s, its toxicity by valence state was appreciated for the biosphere. However, its multipolltuant interactions, from emissions to deposition, were not understood. The case for regulating mercury was assembled in the United States and Canada in the 1990s (e.g. EPA 1997; EPRI 1994). These mercury reports, subsequent research, and knowledge of emission control options, informed decision-makers about the potential risks of mercury in the environment and the options for control of this pollutant. This information resulted in U.S. administrative initiatives for emission control of incinerators and later coal-fired power plants. Research on the complexities of mercury deposition in terms of modeling and monitoring in North America continues as the need for future regulatory action is considered.

12.7 Conclusions

The five examples included in this chapter provide a history of North American experience in the management of individual pollutants. In each case, management began with identification of the hazard posed by the pollutant and establishment of a protective standard, identification of the sources that needed to be controlled, model-based estimates of the emissions reductions (both which ones and by how much) needed to reach the standard, and assessment through ambient measurements of the success of emissions reductions that were achieved. This sequence of activities follows the first two to three steps in the accountability chain illustrated in Figs. 3.1 and 3.2. In some cases, particularly with respect to PM management, attempts have been made to address the last two links of the accountability chain by determining whether or not actions that have been successful in reducing ambient concentrations (or deposition) have been successful in improving public health (or ecosystem function). Especially in the case of public health, these analyses have been limited by incomplete information on exposure, and the assumption has had to be made that relatively large-scale characterization of ambient concentrations is an acceptable surrogate to actual exposure and dose. Even so, there is emerging weight of evidence that reductions in ambient concentrations of pollutants, especially particulate matter, have resulted in positive public health outcomes such as reduced mortality.

In each of the illustrated cases, multipollutant considerations have been present but limited in extent. The principal exceptions have been in coordination of urban-scale emissions reduction actions for achieving management goals for ozone and PM_x (see below), and in the coordination of SO_x and NO_x emission reductions for reducing acid rain and for achieving regional air quality goals for ozone and PM. On the other hand, some of the cross-linkages between accountability and the management process envisioned in Fig. 3.2 have occurred. Air quality management plans have been revised when observations indicate that the projected goals cannot or will not be met.

The examples in this chapter illustrate that current air quality management practice in North America is being conducted at *Levels 1* or *2*, as described in Sect. 3.3.1. Recently, experiments in southern California (SCAQMD 2007) and Georgia (Cohan et al. 2007) have moved toward *Level 3*. EPA's demonstration project in the Detroit metropolitan area has explored a risk-based approach that attempts to integrate management of ozone, $PM_{2.5}$, and certain HAPs (Wesson et al. 2010). This experiment suggests that such an optimized approach could substantially reduce the cost of achieving air quality management goals as compared to a single-pollutant approach.

The five case studies in this chapter illustrate the capability to achieve at least the linkages between emission changes and changes in ambient air quality. Beyond this accountability step, tracking exposure to and effects on humans and ecosystems remains problematic. A complete analysis of the risks to air pollutant exposure envisaged in Fig. 3.2 could substantially enhance decision maker guidance for effective and efficient air quality management.

With today's knowledge, and as illustrated by the five case studies, we can say that:

1. Resources exist to characterize the complex chemistry of the CPs, and to some extent the HAPs.
2. Measurements exist to track long-term trends in ambient concentrations of criteria pollutants in urban locations in the United States and Canada, with less capability in Mexico, except for Mexico City. Tracking of trends in HAPs is restricted to a subset of the total 187 listed in the United States and Canada and is generally not done in Mexico.
3. Long-term changes in ambient concentrations have not been compared with the initial projections from air quality models used to design management strategies. The comparison of emission changes with ambient concentration changes is inhibited by the evolution of emission characterization methods and ambient measurement technologies. However, opportunities could be fostered for such comparisons using a combination of prospective modeling analyses designed into major management initiatives.
4. The ability to characterize the human health and ecosystem effects of exposure to pollutants has improved substantially in the last two decades. However, the

tracking of improvements in human or ecosystem health from pollutant exposure or from deposition remains problematic even for the single pollutants, given the practical difficulties of tracing epidemiological and toxicological markers of change.

The case studies show that current knowledge could support a performance- and relative risk-based multipollutant air quality management approach:

1. A knowledge base exemplified by the five examples provides a reasonable starting point in the atmospheric sciences and emission characterization to move towards formalizing a multipollutant air quality management approach.
2. The association of changes in emissions with changes in ambient air quality or deposition provides qualitative confidence in our ability to assess how management decisions have reduced outdoor human or ecosystem exposure levels. The strongest evidence for links between emission reductions, ambient concentrations, and improvements in public health have been demonstrated for primary pollutants that are non-reactive or slowly reactive in the air, and for fine particle mass concentration.
3. Characterization of exposure and human response to either single or groups of pollutants remains the most incomplete of the elements needed for risk-based air quality management. If a performance or accountability based approach, including complete risk analysis, is to be designed at a *Level 3* or *4*, then risk characterization requires a significant effort in order to implement a complete risk-based management system.
4. Characterization of the exposure and response of vulnerable ecosystems to single or groups of pollutants has improved substantially for aquatic ecosystems, but remains problematic for terrestrial systems. This element of multipollutant air quality management appears to be adequate for single pollutant air quality management, but may be limited for multipollutant air quality management applications as foreseen in this study.

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Chapter 13
Toward Risk- and Results-Based Multipollutant Air Quality Management—What's Next?

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This assessment has been written with certain assumptions about the nature of a multipollutant air quality management framework that could supersede the current single pollutant regulatory framework, particularly in the United States. The present management framework was established decades ago, and has increasingly employed multipollutant considerations in managing pollutants such as ozone and $PM_{2.5}$. Changing established policies and procedures to formalize a multipollutant air quality management strategy will necessitate significant effort over a period of time, as exemplified by the hypothesized four levels of transition in the United States, described in Chap. 3. Parallel hypothetical transitions for Canadian and Mexican policies have not been included specifically in this report. However, analogous approaches to multipollutant air quality management in Canada and Mexico could follow a similar transition path.

That the effectiveness and efficiency of air quality management could be improved through implementation of a multipollutant approach remains unproven at this point. It is also unclear that such a comprehensive approach would indeed achieve the goals proposed by the U.S. National Research Council (NRC 2004) report, or by this assessment. The response to the NRC recommendations in the U.S. has focused primarily on addressing them within the existing management process from standard setting to the calendar for planning and implementation. In fact, it appears that this was the kind of response envisaged by the NRC (2004) Panel.

As we consider what additional actions would need to be taken to facilitate a transition to multipollutant air quality management, it must be recognized that multipollutant considerations are already imbedded in the current single-pollutant air quality management process in all three nations, including risk analysis as part of the regulatory considerations in decision-making. The principal policy question is whether there is a compelling need for going beyond current practices. As discussed here, achieving a fully integrated air quality management structure by source, chemistry, and effects will require substantial investment in new knowledge, especially in terms of the dose-response relationships, that drive risk analyses. Even with the

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commitment of appropriate resources, developing the knowledge base for supporting full implementation of risk- and results-based multipollutant air quality management will take a considerable period of time.

In the meantime, substantial progress could be achieved within the current single-pollutant air quality management framework. Retrospective research into the effects of past emission reductions on ambient air quality would be useful in assessing current abilities to conduct accountability studies. In addition, additional research is needed to assess ambient air quality as an indicator of exposure and to find a credible means of establishing a public health measure of the improvement resulting from changes in ambient air quality. An adjunct to this human health metric would also include more in-depth investigation of the responses of aquatic and terrestrial biota to reductions in the ambient concentrations and deposition of pollutants. These advances should be within the reach of today's technical resources. Pursuing this research agenda should be a high priority for CPs and for selected HAPs where the record of emissions, model projections, and ambient observations is well established.

A transition from today's regulatory practice to a complete, risk-based, results-oriented multipollutant management strategy would be a major challenge for North American air quality management. If such a path is chosen, the transition to this approach might occur along the lines proposed in Sect. 3.3.1 with four levels of change. The current approach to air quality management, which is embodied by *Levels 1* and *2*, has resulted in major improvement in air quality as exemplified in Chap. 12. The purpose of this chapter is to comment on the status and limitations of the current tools for achieving higher-level multipollutant air quality management and accountability (*Levels 3* and *4*). Progress towards these higher levels of practice depends on obtaining the appropriate exposure, health, and ecosystem effect metrics, combined with the tools needed to address multipollutant combinations. The remainder of this chapter focuses on a proposed research and development agenda for supplying, over the next decade or so, the additional knowledge needed to support a risk- and results-based multipollutant air quality management strategy. This agenda includes some initial, near-term, experimental study designs that could facilitate the development of this approach.

13.1 Resources for Air Quality Management and Accountability

Many of the basic technical resources needed to implement a multipollutant approach to air quality management already exist. These capabilities and their limitations are described in Table 13.1. The principal missing ingredients are better information on exposure, dose and risk for single and multiple pollutants, and the modeling and observational information needed to support more accurate estimates of exposure for risk assessment and accountability analyses.

Table 13.1 Summary of tools and capabilities currently available for application to multipollutant air quality management

Requirement	Status	Limitations	Comments
Emissions	Emission estimates for CPs are available but are uneven in reliability. The HAPs inventory applies to some species, but generally not all. Where multiple species characterization is needed (e.g., VOCs and PM_x), emission data have to be extrapolated from limited knowledge. Large stationary sources are reasonably well characterized, and extensive models exist for estimating emissions from motor vehicles and to a much less extent for area source components. Inventories have evolved without concern for historical consistency	Emission characterization is perhaps most reliable for electric power production in the United States. It is less reliable for other sources, especially area sources. Emission development has followed closely the needs for regulated pollutants, especially CPs. Less attention has been given to reliable HAP inventories, as with the chemical composition of various emissions (VOC and PM_x). Inventories are not fully compatible in time or space, and they frequently lack the temporal and spatila resolution needed for exposure estimates. These limitations make accountability estimates problematic. The inventories do not provide for reliable projections and account for changes in technology, land use, and transportation only in a limited way. The projections generally are not verified retrospectively either at the local or national level	Emission estimation remains central to the quality of information available to the decision maker. A transition to multipollutant air quality management will place more stringent multiple pollutant requirements on emissions, as will accountability. This needs to be considered with other needs for air quality management effectiveness and efficiency. Accountability will require increased attention to traceability of emission estimates from year to year as part of documenting emission reductions compared to projections from strategic plans. Development of a multipollutant paradigm will require much more effort to provide speciated emission estimates, in combination with attention to comparability in time and space
Measurements	Focus on CP monitoring and to a much lesser extent surveillance of some important air toxics. Monitoring programs have been designed for many applications, but they are strongly oriented toward regulatory compliance. In practice the system is limited by available funding resources. Short term campaigns have added valuable data for process studies, but are expensive adjuncts to basic monitoring	National monitoring programs concerned mainly with CP monitoring, and intermittent surveillance of HAPs. Conceptual considerations for multiple spatial and temporal scales have been considered, but without priority for implementation. Programs for systematic trend monitoring are limited to selected CPs and HAPs. Capability to track source-ambient air quality response across multipollutants is limited, and is not coupled with retrospective or prospective modeling. Determination of dry deposition of species remains problematic relative to ambient concentrations and wet deposition	National requirements differ substantially. Instrumentation could be available to obtain a large suite of CPs and HAPs together, but the cost would be high, and the multipollutant network requirements for existing locations have not been evaluated. Within current or declining resources, multipollutant requirements need to be specified for long-term measurements in space and time commensurate with needs for compliance and applications from compliance to forecasting and concentration gradient determination

Table 13.1 (continued)

Requirement	Status	Limitations	Comments
Air Quality-Effects System Models	Integrated system models[a] do not exist even for single pollutants, but rely on air quality models for exposure projection. Multi-pollutant air quality models now are available for ambient concentration and deposition estimates. Calculations are done on multi-spatial and temporal scale. Models continue to evolve with improved atmospheric process knowledge, but traceability of history of projections is limited. Quantitative trend analyses of projections vs. measured change in ambient concentration generally have not been attempted even for single pollutants or for combinations of reactive species	Health and ecosystem response models are decoupled from air quality models at the ambient concentration and deposition estimates. Air quality management is relied upon extensively for estimation of ambient concentrations. Some empirical models exist coupling these to exposure estimation for populations. This system has variable reliability depending on the pollutant addressed, especially for organic components. Models are limited by input data and are sensitive to emissions estimates and multi scale meteorological phenomena. Cloud processes are not reliable from first principles, but use extrapolated measurements of cloud cover, depth and precipitation. Local scale (< 5–10 km) calculations, which are most relevant for exposure estimation, are problematic, and present significant quantification issues for HAP exposure	It's unclear at this juncture how important fully integrated system modeling is for regulatory purposes. The current method of separating the air quality management output from the biological or ecological response models is workable well into the future. There is promise for interfacing air quality model output with exposure estimation across populations. This is required before air quality management output can be linked properly with biology-based health response models. Also important will be continuing the efforts for process oriented and empirical models to more fully incorporate CPs and at least a subset of HAPs with more or less equal reliability in the calculations. To achieve this goal, field measurements of non-conventional reactants and products will be needed. Expansion of intercomparisons of model projections and measurements will be needed for trend analysis and feedback to planning. Model forecasting and measurement comparisons may facilitate addressing this need

Table 13.1 (continued)

Requirement	Status	Limitations	Comments
Health Effects	Major focus on ozone and PM_x (multipollutant) properties; improved ozone studies. Some knowledge of cumulative-additive exposure effects and source-health relationships. Concentration-response relationships projected mainly for CPs and less for HAPs. Improved knowledge of exposure response mechanisms for single pollutants exists, but total exposure not accounted for—focus on outdoor conditions	Multipollutant-based dose-response relationships are beyond the current capability of health studies. Determination of long term trends in health relevant to air pollution generally is beyond the reach of health studies. Controversy continues about the severity of health impacts at current ambient concentration levels. Exposure modeling recognizes indoor–outdoor and activity distinction, but is rarely accounted for in risk assessment. Integration of dose response, exposure-response, or concentration-response for CPs and HAPs differs fundamentally, and needs to be integrated	Initial steps toward establishing a multipollutant air quality management paradigm will necessarily need to codify the effects of groups of pollutants and their effects. This in turn will require investment in refined designs for health effects studies, well beyond today's single pollutant emphasis. Feasibility studies to explore the implications of such new designs for additive and synergistic effects of pollutant exposure, are warranted to establish a direction for coordinated studies in the future
Ecological Effects	Focus is mainly on acid related deposition, ozone exposure and Hg deposition for unmanaged ecosystems. Managed systems including agriculture have similar emphasis. Watershed-soil-forest models exist for predictions. Phenomenological knowledge of effects exists for vulnerable systems. Good knowledge of trends in freshwaters with pollution control of acidity and ozone, but poor for mercury in aquatic systems at present	Multipollutant exposure of ecosystems concern acid forming species, and the influence of certain metal combinations. Characterization of ecosystem effects from pollutant exposure is limited relative to CPs and HAPs. Ozone is treated separately from nitrogen species, even though there are direct chemical interactions between oxidant chemistry and acid deposition. Relatively little attention is given to quantitative analysis of modeling projections vs. measured response, especially in terms of biomarkers for aquatic and terrestrial systems.Accounting for dry deposition is problematic relative to wet deposition	Dealing with ecosystem stress from air pollutant exposure has been at much lower priority than the human health driver. Broadening the scope of study of air quality impacts on aquatic and terrestrial systems will continue to be lower priority for U.S. decision makers. Agricultural concerns largely have been dealt with by production of exposure resistant hybrids in Canada and the U.S., though this is less clear in Mexico. Freshwater fish populations were managed as in the past for recreational concerns. Endangered and protected species are only now being considered for control needs. Protection of species is a cultural issue extending well beyond near-term human centric concerns

Table 13.1 (continued)

Requirement	Status	Limitations	Comments
Risk Assessment	Risk assessment tools are available for single pollutants, and some regulatory combinations common to combustion sources. Focus has been largely on cost-benefit tradeoffs, and not on pollutant priority tradeoffs. Methods depend heavily on damage or concentration-response functions. Target and critical loads are available for pollutants impacting some ecosystems	The reliability of comparative risk assessment depends critically on the reliability of component models or concepts. Risk estimates and their significance to priority setting for air quality measurements depend on not only air quality management, but the concentration-response or dose-response estimates from the effects community. The formalities of risk assessment and decision risk estimation are far advanced beyond the input data they require. To implement a relative risk methodology, the single pollutant concentration-response relationships will need to be recast for multipollutants; early on the difference between the HAP and CP risk methodology needs to be reconciled	Risk assessment and management principles have considerable appeal for technically oriented advisors of decision-makers. For non-threshold effects, which current evidence suggests are the case for population effects of CPs, risk quantification is perhaps the only alternative for considering target concentrations and emission levels. The opportunity to objectively develop priorities for pollution management by effects "impact" is an ideal unachieved to date.If multipollutant air quality management and accountability can provide for such a framework, a proposed transition will be welcome to stakeholders. Extending the output of models to economic terms is desired and undertaken but the results are controversial
Climate Change Interaction	Climate change will influence air quality and vice versa. Some recent studies using modeling have explored the ozone and PM_x relationships, identifying complications for health and ecological effects	Climate forcing from greenhouse gases and particles has long been considered relevant to air quality policy in Canada and Mexico. Recently these elements have been determined to be within the framework of the U.S. CAA. Addressing climate related emissions formally could be part of multipollutant air quality management considerations. These encompass spatial and temporal scale phenomena generally excluded from U.S. regulatory considerations. Climate relevant issues will be required as part of future knowledge requirements. Combining air quality and climate models is underway; early model versions are being tested as a means of examining various air quality and climate interactions	To date, the direct effects of human induced climate change have largely driven considerations for addressing the climate issue. The interactions with air quality appear to be "second-order" and very long term relative to achieving present day goals. While there is a need to provide for the uncertainties in demography associated with climate change, it may continue to be a lower priority than simply dealing with air quality in a traditional way. Integrated risk assessment will be essential to determine priority setting on the climate interaction scale

Table 13.1 (continued)

Requirement	Status	Limitations	Comments
Integration for Decision making	Integrated considerations for multipollutants are largely focused on air-chemical processes of NO_x and VOC, and SO_2. Integration of the regulatory calendar and planning for different CPs is in test in the United States. Multipollutant interactions are considered only in a limited way in Canada and Mexico, in conjunction with ozone and PM_x. reduction strategies	Single pollutant air quality management is strongly imbedded in North American air quality management practices. The Canadian and Mexican regulatory approaches generally are more flexible than the U.S. policies. However, the economic resources for dealing with air quality at high public priority in these countries are more limited. To move beyond making the regulatory calendar and parallel management of single pollutants, a multipollutant air quality management paradigm will require significant improvement in knowledge not available today. The transition to multipollutant air quality management hypothetically could involve several years with organization to achieve different levels of sophistication in approach. The tools for achieving this level of completion are not available	Integration of pollutant management for decision making will likely become a stronger driver as the costs to the public for environmental protection get larger, and the requirements for air quality as measured by today's standards become more stringent. A risk-based multipollutant air quality management paradigm may lead the way to improved relative risk decision-making, but its potential for improving effectiveness and efficiency needs to be demonstrated with early exploratory experiments

[a] Integrated system models are defined as the formal combination of air quality models, exposure and health-and/or ecosystem response models

Other questions that need to be resolved before embarking on the transition to a risk- and results-based air quality management include whether (a) a risk-based approach is feasible or practical within current knowledge and regulatory practice and (b) a multipollutant air quality management approach is actually more effective and more efficient than the current practice. A study of the feasibility of transitioning from current practice to *Level 3* and *4* air quality management would need to address these questions as well as identify the specific gaps in knowledge (and their priorities) that limit our ability to effect risk-based multipollutant air quality management, and how these gaps might be filled either by experiment or by inference from available knowledge. A part of this feasibility study would include (a) a comparison between the effectiveness of a multipollutant air quality management approach and a single pollutant management approach for a specific area, and (b) how grouping of pollutants to achieve a set of specific goals could be done effectively. Such a study could be conducted within the current regulatory frameworks[1] of all three nations of North America. The strengths and weaknesses of a risk- and results-based multipollutant management approach could be estimated, and policy alternatives could be explored. At the conclusion of this exercise, a decision could be made concerning the value of investing in a transition to a multipollutant air quality management, and the specific research and development needed to support it could be identified.

Future studies should also include evaluation of our current ability to implement accountability as described in Chap. 3 of this assessment. This evaluation should address questions such as (a) how far down the accountability chain is it feasible to go given current emissions and monitoring information, (b) what changes to current emissions inventories and monitoring methodologies are needed to support more in-depth accountability (e.g., to the levels of evaluating changes in exposure and resulting improvements in human and ecosystem health), (c) can accountability be used to provide "mid-course corrections" to air quality management actions as they are implemented, and (d) what is the feasibility and value of retrospective accountability studies for providing insights into the effectiveness of past air quality management actions and how can these insights improve future air quality management decisions.

13.2 Research and Development Planning for Multipollutant Air Quality Management

As mentioned previously, the U.S. regulatory program could evolve over the next several years towards a multipollutant air quality management approach embodying integration of CP and HAP strategies. Recently, some states have begun responding to state implementation plan (SIP) requirements for ozone and $PM_{2.5}$ by treating

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[1] A legal structure for a fully developed multipollutant air quality management with binding regulations and enforcement policies remains to be conceived. Such a structure is beyond the scope of this report.

them as multipollutants (e.g. Cohan et al. 2007; SCAQMD 2007). EPA has also started experimenting with multipollutant test programs of this kind in three states, with a focus on optimizing risk reduction for ozone, $PM_{2.5}$ and certain HAPs. An example of this *Level 3* approach was recently attempted in Detroit, Michigan, using existing knowledge and modeling methods.

13.2.1 The Detroit Multipollutant Pilot Project

The U.S. EPA Detroit Multipollutant Pilot Project was conducted to test the concept of developing a comprehensive air quality management plan for simultaneous reduction of ozone, $PM_{2.5}$, and toxic air pollution and to inform participating state and local agencies about the technical methods, tools, and models for achieving integrated policy development. The Detroit metropolitan area was identified as a good candidate for testing such a strategy given the existence of multiple pollutant issues within the region[2] and the availability of a relatively rich observational database that combined conventional monitoring with supplementary information from the Detroit Exposure and Aerosol Research Study,[3] the Detroit Air Toxics Initiative, and the Detroit Children's Health Study.

In setting up the study, a future 2020 baseline condition was developed that accounted for projected economic growth and "on-the-books" or mandated control programs. Two emission reduction strategies were then developed to meet ozone and $PM_{2.5}$ NAAQS within the Detroit area. One strategy was a conventional approach where controls were selected to address ozone and $PM_{2.5}$ nonattainment independently. The second strategy was an integrated multipollutant, risk-based approach that emphasized achieving simultaneous reductions in population risk from exposure to ozone, $PM_{2.5}$ and selected air toxics of interest in Detroit (naphthalene, methylene chloride, manganese, cadmium, nickel and diesel exhaust PM), while still addressing ozone and $PM_{2.5}$ nonattainment.

The two emission reduction strategies were input to a multiple pollutant air quality modeling system[4] that produced local, fine-scale (~1 km horizontal resolution) simulations air quality concentrations for the urban core of Detroit and regional (~12 km horizontal resolution) ambient concentrations for the surrounding area. For each strategy, the human health benefits were estimated from the resulting changes

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[2] As summarized by EPA (2008), the Detroit metropolitan area is classified as nonattainment with respect to ozone and $PM_{2.5}$. The 2001–2003 derived design values were 19.5 μg/m^3 (relative to 15 μg/m^3 1997 annual standard) and 0.097 ppm (relative to 0.085 ppm 1997 8-hr standard, respectively). In addition the Michigan Department of Environmental Quality reported that at least thirteen air toxics in the Detroit urban area could be contributing to the majority of the total HAPs risk (http://www.michigan.gov/deq/0,1607,7-135-3310_4105-139044–,00.html.).

[3] http://www.epa.gov/dears/studies.htm.

[4] Wesson et al. (2010) provide details on this system composed of results from the EPA's Community Multi-scale Air Quality (CMAQ) photochemical model (Byun and Schere 2006; Byun et al. 1999) and the AERMOD Gaussian dispersion model (EPA 2004).

in the ambient concentrations of CPs and air toxics. As a performance metric, benefits were monetized for population exposure, and the changes in cancer and non-cancer risks were compared with the total costs of controls. Both local and regional changes in air quality concentrations for ozone, $PM_{2.5}$ and air toxics of concern were compared for the two control strategies.

Comparison of the two strategies showed that the multipollutant, risk-based approach achieved NAAQS attainment goals for ozone and $PM_{2.5}$ that were similar to the conventional approach but the multipollutant approach achieved greater reductions in exposure and risk for all pollutants considered (i.e., ozone and $PM_{2.5}$ attainment and the HAPs) as is shown by the following results:

1. *Improved ozone and $PM_{2.5}$ air quality:* The multipollutant, risk-based approach was able to achieve equal or greater reductions in $PM_{2.5}$ and ozone at the monitoring locations, with all $PM_{2.5}$ concentrations at the monitors being below 15 μg/m^3 and all ozone concentrations being below 85 ppb. The multipollutant approach showed a maximum $PM_{2.5}$ difference of 2.3 μg/m^3 and an ozone difference of 0.2 ppb as compared to the conventional approach.
2. *Improved air quality for ozone, $PM_{2.5}$ and selected air toxics across the metropolitan area and urban core:* As shown in Fig. 13.1, the multipollutant risk-based approach realized greater regional and local air quality improvements in ozone and $PM_{2.5}$, and it achieved greater reductions in concentrations of key air toxics in the Detroit urban core.

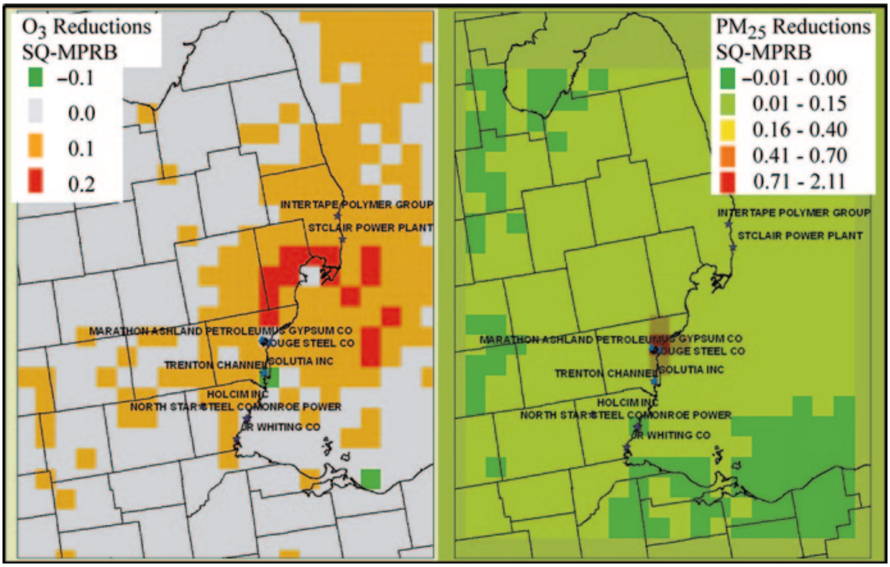

Fig. 13.1 Illustration of the southeast Michigan air quality difference maps for 4th highest ozone (ppb, *left*) and Annual Average $PM_{2.5}$ (μg/m^3, *right*). Differences in air quality were developed by subtracting the 12 km concentration fields of the MPRB from the "status quo" strategy. (Source: R. Scheffe—personal communication)

Table 13.2 Comparison costs and benefits for the MPRB and "status quo" strategies. (Source: R. Scheffe, personal communication)

		"Status quo"	"MP risk-based"
Total benefits (M 2006$)		*$ 1,127*	*$ 2,385*
Change in pop-weighted	Regional	0.16	0.1666
$PM_{2.5}$ Exposure (μg/m^3)	Local	0.2703	0.7211
Change in pop-weighted	Regional	0.0005	0.0006
ozone Exposure (ppb)	Local	0.0318	0.0583
Total costs (M 2006$)		*$ 56*	*$ 66*
Cost per μg/m^3 $PM_{2.5}$ reduced		$ 0.50	$ 0.32
Cost per ppb ozone reduced		$ 2.6	$ 0.58
Net benefits (M 2006$)		*$ 1,071*	*$ 2,319*
benefit-cost ratio		*20.1*	*36.1*

3. *Greater health benefits for $PM_{2.5}$ and ozone controls:* The multipollutant risk-based approach provided more than twice the monetized health benefits from reduced exposure to ozone and $PM_{2.5}$ ($ 2.4 billion vs. $ 1.1 billion), based on application of EPA's Environmental Benefits Mapping and Analysis Program (BenMAP).[5] This outcome was driven primarily by the higher population-weighted change in $PM_{2.5}$ exposure resulting from the multipollutant approach (0.72 μg/m^3 vs. 0.27 μg/m^3).
4. *Reduction in total cancer and non-cancer risk:* The Human Exposure Model-3 (HEM-3)[6] showed insignificant differences between the two strategies for total cancer risk. However, for non-cancer risk, the multipollutant approach resulted in a 30% reduction in population non-cancer risk above the hazard index of 1. The greater reduction in non-cancer risk was mostly due to reductions in manganese emissions from steel mills.
5. *Greater net benefits and cost effectiveness for the overall strategy:* As shown in Table 13.2, the total cost of the multipollutant risk-based approach was somewhat higher than the conventional one ($ 66 million vs. $ 56 million), but the estimated net benefits were much greater for the multipollutant approach ($ 2.3 million vs. $ 1.1 million). Also, the cost per μg/m^3 and ppb reduced was significantly lower for the multipollutant risk-based approach ($ 320,000 vs. $ 500,000 per μg/m^3 $PM_{2.5}$ reduced and $ 580,000 vs. $ 2.6 million per ppb ozone reduced). Finally, the mulitpollutant risk-based approach showed a far more favorable benefit-cost-ratio than the conventional one (36.1 vs. 20.1).

This study represents a first demonstration that a risk-based multipollutant approach to air quality management might offer real advantages compared to conventional single-pollutant management. It suggests that the multipollutant approach

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[5] The BenMAP model (Abt Assoc. 2008) estimates ozone and $PM_{2.5}$ human health benefits for an array of health endpoints, including mortality, chronic bronchitis, non-fatal heart attacks and a variety of acute endpoints including asthma attacks.

[6] Alpha-Gamma Technologies (2007).

is capable of meeting multiple emission reduction criteria, while achieving gains in both efficiency (i.e., cost-effective pollutant reductions) and risk reduction (as reduced population exposure for all included pollutants). However, these conclusions are based on modeled results and not on observations or verified cost and risk reductions. Actual verification of the relative success of the multipollutant approach would require application of a true accountability assessment based on measurement-derived exposure estimates and, perhaps, epidemiologically derived risk reductions. Nevertheless, even in the absence of a data-driven accountability assessment, the robustness of the Detroit conclusions could be tested by additional model-based analyses of (a) the sensitivity of the results from emissions and other model inputs, (b) the potential for the air chemistry of naphthalene and methylene chloride (or ozone-$PM_{2.5}$ chemistry) to produce unaccounted-for toxic products, (c) the uncertainties in concentration-health response relationships used in BenMAP, especially for neighborhood concentration variations and meteorological features, and (d) the ambiguities in monetizing relative benefits for risk reduction of each of the each of the pollutants considered.

Although the Detroit study suggests advantages in a risk-based multipollutant approach, further advancements depend upon the filling of important knowledge gaps and the development of improved exposure assessment and risk-reduction tools. For example, additional progress depends on further development of health and ecological effects concentration-response profiles for single pollutants along with justification for the assumption that total risk is derived from the sum of individual risk. Further progress also depends upon the development of emission inventories or models for multiple pollutants by source, for example, speciation of VOCs and PM_x constituents, along with air toxics, expanded air quality-exposure models for groups of multiple pollutants to cover a range of spatial and temporal scales, and a formal scheme for optimizing relative risk reduction beyond current capabilities. A risk communication scheme is needed that can inform stakeholders of the options for pollutant management with specified uncertainties and limitations imbedded in the estimates. Formal procedures are also needed for retrospective analyses to provide feedback on the differences between actual long-term measurements and model projections of expected changes in ambient concentrations or exposures compared with actual and expected changes in emissions.

13.2.2 Toward Results-Based Multipollutant Management

Development of the knowledge needed to achieve multipollutant air quality management will require closely coordinated research and research applications from various science disciplines, including engineering (emissions, technology projections and controls), atmospheric sciences, and health and ecological sciences. Table 13.3 suggests a research agenda for obtaining the portfolio of knowledge needed over the next decade or so to achieve true risk- and results-based multipollutant air quality management. Execution of this research agenda, in concert with continuing dem-

Table 13.3 Technical initiatives supporting multipollutant air quality management

Regulatory framework	Transition level tools	Program initiatives
Levels 1 and *2*. Continue present framework for CPs and HAPs, including goal setting. Implement uniform regulatory calendar for CPs Expand weight of evidence techniques for goal setting and achievement. Design and implement accountability components to regulatory strategies. Incorporate human health and ecological objectives for current single pollutant goals	– Weight of evidence, emissions, multipollutant models and measurements for emission reduction strategy. – Evidence of health and ecological effects; concentration-response data for some pollutants – Risk models for single pollutants, and some multipollutant systems. – Capability to conduct retrospective analyses of projections and actual changes for some pollutants	– Improve emissions characterization for species (especially VOC and $PM_{2.5}$); Develop means of continuity in emission data for retrospective analyses. – Improve models oxidants $PM_{2.5}$ and HAPs for spatial representation from neighborhood to regional scales. – Strengthen monitoring to insure long term data for accountability and retrospective analyses; Improve VOC and odd nitrogen data collection. – Improve ambient level toxicity vs. concentration-response relationships for HAPs. – Improve methods for determining change in health and ecosystems for accountability
Level 3. Employ risk analysis for establishing a risk-optimization approach for goal setting in selective cases for ozone-$PM_{2.5}$, and for key HAPs by city. Evaluate alternative structure of goal setting and achievement to enable or clarify changing basis for air quality management from ambient CPs standards and emissions (HAPs) to performance measures gaining reductions and benefits in risk reduction, and changing distinctions between CPs and HAP groupings (rearranging) listed pollutants or creating alternatives in terms of groupings common to sources, chemistry or effects. Evaluate whether effectiveness and efficiency gains in pollution management are justified to change to a *Level 4* multi-pollutant management paradigm	– Increase emphasis on total exposure to known pollutants and establish improved exposure-health and ecological risk paradigms. – Incorporate into model use translation from ambient concentrations to an exposure measure. – Investigate toxicology of pollutant mixtures for additive and synergistic measures. – Incorporate formal retrospective analyses in accountability chain, with feedbacks to strategy modification as needed for ozone, $PM_{2.5}$ and key HAPs. – Incorporate health and ecological improvements. – Incorporate considerations for role of greenhouse gases in modifying projections and retrospective analyses of accountability change	– Conduct in-depth studies to evaluate a basis for multipollutant risk-based health effects relationships and the potential for using these in an accountability framework. Begin these studies with oxidant measures.$PM_{2.5}$ components, and HAPs related to these two CP categories. – Conduct a series of studies aimed at establishing credible exposure measures taking into account indoor-outdoor and activity patterns in different parts of North America. – Expand the accountability studies to trace current strategies for oxidant and $PM_{2.5}$ reductions from emission changes to apparent reductions in exposure and consequent improvement in health effects

Table 13.3 (continued)

Regulatory framework	Transition level tools	Program initiatives
Level 4. Revise legal structure to accommodate emission and pollution reduction strategies that are recommended by multipollutant air quality management. Consider a shift toward relative risk evaluation as part of the standard setting process (including evaluation of groups of CPs and HAP). Move toward North American (international) harmonization of pollutant air quality management based on national and international considerations, and a multipollutant air quality management paradigm	– Coordinate strategy development by a formalized risk-benefit approach, which optimizes benefits for emission reductions. Method would use the tools developed from *Levels 1–3* support, taking into account synergies in health and ecosystem response. – Establish a modified accountability system to conduct retrospective investigations of the multipollutant strategies projected, and their success in reducing environmental risk	– Develop an integrating framework for employing advanced elements of "weight of evidence" information from modeling, measurements and health and ecological effects exposure-response relationships. Integration would be determined through a risk-benefit decision-making framework. – Establish and test a credible methodology to complete the accountability change beginning with pollutant management strategy implementation through measurements of exposure and health and ecosystem changes to risk reduction with feedback and feed forward methods in strategy development. – Incorporate a method for accounting for climate change interactions with air quality as needed

onstration projects that could build upon the experience gained through the Detroit project, would lead to development of the U.S. air quality management process beyond the vision of the NRC (2004). Whether or not such an ambitious program and schedule could be achieved within available resources and schedule, however, remains to be seen.

The following sections of this chapter describe priority aspects of this research agenda in more detail. We recognize that as additional research is performed, and as the recommended test applications of risk- and results-based multipollutant air quality management are conducted, additional research priorities will emerge. The research initiatives discussed here are those that have emerged thus far as being especially important to effecting a transition to a new paradigm of air quality management.

13.2.3 Priority Research and Development Initiatives

To facilitate movement toward a multipollutant management approach, three key issues should be investigated early on. These are (a) a study of and decision on the feasibility of grouping pollutants for practical application of a multipollutant approach; (b) determination of our ability to conduct retrospective analyses of modeling projections of ambient concentrations or exposure vs. actual ambient concentration distributions; and (c) exploration of the application of relative risk estimation for priority setting of human and ecological effects using current information. In the near term, a risk-based strategy for air quality management is probably most sensitive to the risk characterization element, embodying health and ecological exposure response. Without substantive, credible information to develop ambient concentration-response relationships, neither a single pollutant nor a multiple pollutant strategy can employ relative risk assessment.

Evaluation of Pollutant Grouping. As a practical matter, evolution to a complete multipollutant concept would be facilitated if we were able to group pollutants according to some logical basis, such as by source; by chemical reactivity (Chaps. 5, 7 and 8), or by common biological response either in humans or in ecosystems based on existing toxicology and epidemiological results. For example, using criteria[7] relating to respiratory disease, cardiovascular stress, disease mechanisms including cancer or reproductive stress a grouping of various pollutants could be developed which would include both the CPs and at least a subset of HAPs. One approach to grouping by chemistry-health indexes is noted in Chap. 7. An analogous scheme has been used to design toxicological investigation of components of ambient PM by

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[7] These criteria should be firmly grounded in an objective leading to air quality management practices that are "optimally" effective in reducing health and ecological risk. How to accomplish this by combinations of pollutant groups with an appropriate weighting scheme, different identified health effects and ecological effects, separately and combined, remains an open question beyond this study.

source—characterizing a source mixture based on gas and particle components of an aerosol (e.g., Mauderly 2006).

With regard to exposure to multiple pollutants, three possible responses have been hypothesized: (a) no response occurs for a mix of pollutants beyond one pollutant as an indicator, (b) a response takes place which is additive in pollutants present in an ambient mixture, and (c) a synergistic (or antagonistic) response exists wherein the total response is sequential or simultaneous, where the irritation or stress of the mixture exceeds (or is less than) that expected for a sum of single pollutants. If it were possible to group pollutants by mechanism, the conjectures about additivity, synergism or antagonism could be tested through a series of *in vitro* and *in vivo* pilot tests. From these exploratory studies, a more elaborate series of toxicological experiments or human exposure studies could be designed in combination with community health assessments for humans and their ambient exposure to mixtures. In principle, the latter could be facilitated with designs that would include multiple city cases for different climate conditions or pollution mixtures found in North America. Early exploitation of such experiments should be given high priority if a multipollutant air quality management approach is to be developed. In the meantime, much could be gained through analogous experiments focusing on one or more of the single pollutants to further support current management practices.

To explore the concept of biological classification further, a study of this approach involving toxicologists and epidemiologists should be implemented. The results of this work could then be tested by "Delphi" techniques in an expert group organized, for example, by the National Academy of Sciences.

Addressing the Exposure Issue. In addition to an improved understanding of multipollutant effects, advances in risk-based air quality management hinge on improving exposure assessment. This requirement includes not only differentiating between indoor and outdoor exposure, but also characterizing exposure by pollutant groupings on different spatial and temporal scales. Determining combined exposure to CP and HAP groupings as a function of indoor and outdoor conditions and activity patterns is difficult, as is determining urban neighborhood-microenvironment exposure using community-based air monitoring. The application of activity patterns to understanding indoor–outdoor exposure relationships has been investigated in a few cases for CPs, but similar relationships for HAPs are rarely studied. Exposure models such as the ones being developed by Canadian and U.S. investigators could be generalized to address indoor, outdoor, and activity components in relation to the current array of fixed monitoring stations. A research program for developing a generalized exposure model could be designed using literature surveys for a representative set of climate, building practices, and activity patterns by age, gender, and occupation. The design and execution of this kind of program would be the basis for an advanced experimental program on exposure measures (see also Sect. 13.3.1). The research program could also assist in improving the linkage between air quality modeling practice and exposure estimation.

The use of neighborhood scaling to improve exposure estimation based on community monitoring has been explored, but it remains problematic. Understanding neighborhood-scale exposure is difficult because local emissions can be intermittent, or fugitive, in character and not well represented in inventories. More extensive urban studies of local conditions would be helpful in providing insight into this problem. For example, investigations by Blanchard et al. (2006) and Blanchard and Tanenbaum (2007) for PM exposure in Birmingham, AL, and Zhu et al. (2008) for HAPs in the Hoboken, NJ neighborhoods have pointed to the influence of strong HAP concentration gradients in urban conditions, which originate in these cases from local small business or residential emissions superimposed on community-scale background conditions. These studies indicate the importance of improving knowledge about such highly local influences on exposure, relative to a more general urban condition estimated from observations and modeling.

An early action for clarifying the exposure issue would be to design and implement a major study analogous to the Detroit Exposure and Aerosol Research Study (DEARS) (Watkins et al. 2008; Williams et al. 2008), ARIES in Atlanta, GA (e.g., EPRI 2005) or the recent Steubenville, OH Study (e.g., SCAMP; Connell et al. 2007). However, this study would focus on characterizing the relationships between emissions and ambient concentrations of pollutants from the neighborhood to regional scale. It would include representative indoor and outdoor air concentration measurements and activity measurements for target sub-populations. Such a program would be expensive, but it would be a priority investment in clarifying a number of measurement and exposure issues relevant to multipollutant air quality management.

Retrospective Comparison of Model Projections and Ambient Concentrations. Studies already exist that could be used to test the value of existing information for conducting retrospective performance assessments or accountability. Such studies would build on work already done in North America to establish trends compared with estimated emission reductions of certain CPs and HAPs (e.g., as illustrated in the examples cited in Chap. 12). In most of the studies documented in the literature, the accountability chain depicted in Fig. 3.2 is broken in one way or another. Typical breaks include a lack of comparisons between ambient observations or media chemistry with earlier projections from air quality management or ecological models, or a failure to assess specifically the effectiveness of the action by investigating its effect on public health. While the ability to assess direct health improvements remains to be proven conclusively for cases exclusive of sudden reductions in source emissions, a retrospective comparison with air quality management projections could be made for certain pollutants, provided the emission changes and model comparability could be established by design in major emission reduction initiatives (e.g., those listed in Table 8.1). Good examples of recent progress in this area are the trends studies of $PM_{2.5}$ change in association with air concentration changes.

The results of studies of the relationships between health endpoints and changes in ambient PM concentrations so far reported in the literature could be evaluated for areas in which extensive modeling has been conducted in designing the management strategies. These analyses would complement recent work examining the effectiveness of the U.S. (regional) NO_x SIP call for reducing regional ozone concentrations across the eastern United States and Canada (see also Chap. 12).

A candidate for retrospective analysis of ozone and PM control measures is the Los Angeles area. The area has a long record of emission inventory development and air quality modeling and monitoring, and it could easily support such an analysis. There are data going back to the 1970s for ambient ozone and NO_x precursors in the area, as well as intermittent data for VOC composition and PM_x. Furthermore, the area has a long-established emission inventory starting in the 1970s that could be used to compare emission reductions with projections. Since the California South Coast Air Quality Management District has conducted a number of studies of modeling vs. ambient air quality, these results could be reviewed critically and reported. Various health related investigations since the 1960s could be evaluated, using air quality modeling results and spatially diverse ambient measurements for estimating ambient concentrations, to extend health studies reported recently in the literature, or to test previously reported concentration response relationships for change over time (e.g., perhaps the six-city cohort approach of Laden et al. 2006; or the decadal comparison using the NMMAPS subpopulation of Dominici et al. 2007).

Other areas also having a long enough measurement record and a series of SIP projections to support retrospective investigation of concentration/response relationships might include central California, Houston, Denver, the Great Lakes region, or the northeastern United States. These candidates could be examined with local authorities to determine if a thorough retrospective analysis could be productive.

Investigation of Accountability and Health Response. Closing the risk management cycle (e.g., Bachmann 2007) requires establishing that improvements in public health have resulted from improvements in air pollution conditions. The Health Effects Institute has invested in a modest effort to address this question in recent years, with most emphasis on the analysis of intervention studies (e.g., HEI 2003). Expanding on HEI's work, there are opportunities for developing innovative methods that would allow the epidemiological community to improve analyses of long-term community health records and ambient air quality data to gain improved understanding of the health effects of single pollutants. Such investigations could build on the studies of Burnett et al. (2005); Jerrett et al. (2007), and Shin et al. (2008). These investigations have attempted advanced stochastic analyses, using a combination of multiple city and long-term trend analyses of mortality intercomparisons for one or more pollutants, to strengthen epidemiological associations for certain pollutant indicators such as ozone and/or NO_2. The Shin et al. analysis, for example, indicates increasing mortality weighted ozone concentrations trends, but declining NO_2 concentration trends, in 24 Canadian cities over the period 1984–2000. In contrast to the ambient concentration trends, however, the health risk associated with ozone exposure seems to be declining, while the risk from exposure to NO_2 appears to be increasing. If these results are confirmed, the statistical method of Shin et al. might be applied in more elaborate analyses of the relative risks associated with long-term changes in pollutant mixtures.

Other robust statistical methods could be explored to deal more effectively with the time series signal to noise ratio, perhaps along the lines of the theory for separating signal from random noise in telecommunications. Combining the results of intervention studies and "ecological" epidemiology studies also shows promise for improvements. The exploitation of existing air monitoring and health data has expanded recently (see also Chap. 12), including studies of ozone and respiratory and cardiovascular disease in the Los Angeles area. For PM, studies of the health effects beyond lead or sulfate reductions, such as carbon reductions, could be initiated in the Northeast and other portions of the United States. Studies of the health consequences of reductions in CO within urban centers could also be expanded. Development and application of improved methodologies for understanding the health effects of single pollutants is an essential first step in achieving a risk-based approach to ambient air quality management. Once these methods have been tested and documented for single pollutants, the methodology could be extended to multipollutants through the concept of pollutant grouping.

Achieving these goals will require improvement in access to, and relevance of, population health effects data. Coordination is needed between the entities that collect mortality and morbidity data, and the epidemiological and atmospheric science communities. Eliminating current ambiguities in transitioning from concentration-response relationships to dose-response relationships for both CPs and HAPs will depend on improving access to appropriate health data. Diseases such as cancer or respiratory stress from asthma may be too complex for accessing such data in the near future. However, other health endpoints such as COPD or respiratory stress may provide a simpler direction for linking pollutant effects with changes in ambient conditions.

Exploration of Relative Risk Estimation. Given the current risk-based modeling framework, a test of the use of existing information would involve examining the relative risks of exposure to combined CPs and HAPs over a range of known ambient concentrations. Assuming the apparent effects range from response to exposure to single pollutants to additive effects for exposure to combinations of pollutants,[8] one could conduct a hypothetical assessment of the relative risks of exposure to the existing menu of pollutants. This assessment would be instructive relative to the investment in pollution control currently in place. Perhaps an estimate of PM effects could also be obtained for assumed risk according to composition and particle size. Of course there also is a need to assume a relationship between HAP risk criteria (cancer and other diseases) and the CP population exposure and risk. This exercise

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[8] Workers have not agreed on approaches to quantify pollutant risks including single pollutant combinations. The Canadian approach, for example, adjusts acute effects for ozone and NO_2 concentrations. In the United States, this issue remains unresolved in regulatory practice, but researchers continue to estimate risk based on epidemiological treatment of linear combinations of pollutants.

would give conceptual guidance to extension of the risk concept to multipollutant mixtures, assuming only additive effects.

13.3 Additional Priority Considerations

In addition to the topics discussed above, three additional areas require attention if we are to achieve a transition to multipollutant air quality management. These areas are (1) improving air quality measurements and monitoring systems, (2) improving the interface between air quality and exposure modeling, and (3) understanding and taking into account the interactions between air quality and climate.

13.3.1 Improving Measurements and Monitoring Systems

Long-term simultaneous measurements of ambient air concentrations of CPs and HAPs continue to be limited in North America. Current measurement programs are designed to achieve a number of different objectives from compliance monitoring to scientific research. Of necessity, these networks represent a compromise approach to achieving these different goals. Measurement programs are expensive, and each nation is limited in what it can afford.

The measurement needs for accountability testing and multipollutant air quality management are distinct. In the former, self-consistent long-term measurements are required to characterize ambient concentrations and gradients in population centers. In order to achieve future accountability objectives, a broader suite of species measurements will be required in urban and rural areas, as well as improved temporal and spatial coverage to help resolve the different pathways of exposure to multipollutant mixtures.

In view of the recent focus on improving our ability to understand the health effects of air quality management actions, development of a practical observational program for documenting changes in exposure should be implemented to coincide with all intervention studies. In particular, whenever major emission changes are expected, measurements should be designed and implemented within the region of influence of such sources both before and after the change. These measurements should include long-term observations to establish the pattern of ambient change. The use of mobile laboratories could be effective for such exposure studies.

The state of ambient measurements and monitoring networks in the three countries of North America is summarized in Chap. 10. This chapter provides some guidance for improving current monitoring and measurement programs, but it does not address *optimization* of the networks to achieve compliance, accountability, and multipollutant conditions during an era of fixed or declining budgets. The challenge of optimization could be addressed through the use of new instrumentation and multipollutant measurement technologies to replace current reference methods, and through a redesign of programs to incorporate community monitoring with neighborhood concentration gradient studies at selected sites (representing different major source impacts) and short term campaigns to address projected health or ecological impacts. The experience gained in studies from the U.S. supersites program and projects such as ARIES (EPRI 2005) and SCAMP (Connell et al. 2007) should provide input for such designs.

13.3.2 Integrated System Modeling

Improvement of air quality models will continue as knowledge about physicochemical processes occurring in the atmosphere increases. A particular priority for improvement is in the treatment of carbon and organic species in the models. Achieving these improvements is critical to improving the treatment of $PM_{2.5}$ and HAPs. In conjunction with these improvements, improvements in the chemical characterization of the end-products of first and higher generation atmospheric reactions are also a high priority, especially if these products are found or suspected to be toxic air pollutants. Beyond some work on organonitrates as carcinogens, or peroxides as biological response catalysts for oxidative stress, little effort has been devoted to exploring atmospheric chemical end products for their toxicity.

The increasing effort to employ air quality modeling for forecasting and parallel comparison with measurements offers an opportunity to test accountability on a monthly to seasonal basis. This potential could be exploited with prospective health studies to address the accountability chain in a few locations.

Air quality modeling, including exposure estimation, will be central to multipollutant management applications. However, formal integration of air quality modeling and exposure estimation appears to be less urgent to the health-effects community because the current approach of “handing-off” information on ambient concentrations or deposition rates for subsequent assessment of risk appears to satisfy the human and ecosystem exposure-effects communities.

13.3.3 The Effects of Climate and Global-Scale Emission Changes

Exploratory model-based investigations of the influence of climate change on air quality and vice versa have been initiated in the United States and Canada. These analyses depend upon projecting emissions for the next 50 years and beyond, using assumptions of technological change that are likely to become quickly out-of-date. Analyses so far have suggested that the effect of climate change on air pollution is secondary to other air quality management uncertainties. The rate of climate change is still slow compared to the air quality management cycle. Also, investigations to date show that current air quality management approaches will remain effective under a projected changed climate. With respect to the direct effects of climate change on air quality management, there is time to learn and adapt.

Changes in global-scale air quality related emissions could also have significant effects on future air quality management practices in North America. These changes will result from continued economic growth as well as from changes that will be required to reduce greenhouse gas emissions. Changes in emissions on the global scale will affect the background chemistry of the atmosphere, and they will affect hemispheric transport of air pollutants and pollutant precursors. There is already some evidence of increases in the background concentrations of ozone (see Chap. 11) that have implications for risk-based management decisions regarding this pollutant. The ability of models to reflect perceived or projected technological and infrastructure changes in North America over the next 50 years is critical to understanding the long-range implications of these developments. Such changes are envisaged, not only in the area of stationary sources, but also in the transportation sector. These changes are already occurring across the world, especially in Asia.

There are major opportunities to improve knowledge about projected changes in air pollution emissions across the world. These should be examined for equivalent opportunities for natural or intervention experiments to characterize relationships between the onset of emission changes and consequent health or ecological responses. With such a broadened outlook, investigators could observe shifts in multiscale pollution exposure, quite apart from issues of climate change.

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Chapter 14
Conclusions and Recommendations

George M. Hidy, Jeffrey R. Brook, Kenneth L. Demerjian, Luisa T. Molina and Richard D. Scheffe

The overarching conclusions and recommendations of this assessment complete our examination of the needs for technical support of a multipollutant, risk and accountability-based management strategy for North America. We present our conclusions and recommendations in two parts. The first part addresses multipollutant and risk-based air quality management, and the second part addresses accountability. The conclusions and recommendations refer to the technical tools and knowledge needed to support a transition from current approaches to air quality management to a formal risk- and results-based multipollutant air quality management approach as outlined in Chap. 3. They are synthesized from the conclusions and recommendations in Chaps. 4 through 13. Significant conclusions are highlighted in bold type. Recommendations are numbered.

Although the conclusions and recommendations are discussed separately owing to their focus, they are in fact intertwined. Resolution of uncertainties and gaps in knowledge are needed to realize comprehensive multipollutant, risk- and results-based air quality management as envisaged in Chap. 3, including (a) risk characterization and system response information; (b) implementation of supportive measurement programs; (c) evaluation of the impact of accelerated technological change associated with response to climate change; and (d) demonstrations of accountability analyses.

As discussed in Chap. 3, the assessment team postulated a four-level transition from a pure pollutant-by-pollutant approach to a hypothetical risk-based multipollutant approach to air quality management. These levels are summarized as

Level 1. *A strict single-pollutant perspective with focus on attainment of individual ambient standards.*

Level 2. *Attainment of standards for individual pollutants, but with increasing attention to co-benefits attainable through coordinated emission reductions.*

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Level 3. *Management decisions based on achieving greatest risk reduction based on single-pollutant exposure-dose-response relationships.*

Level 4. *Management decisions based on achieving greatest risk reduction based on multipollutant exposure-dose-response models.*

Within this context, an accountability analysis could be implemented through a series of steps frequently called the accountability chain. These steps incorporate various measurements and analyses for determining whether:

1. The management action was implemented as designed and the expected emission reductions have taken place.
2. The actual or estimated emission changes resulted in the expected changes in ambient concentrations or deposition.
3. The changes in ambient concentrations or deposition have resulted in reductions in exposure of humans or ecosystems to the pollutants in question.
4. These reductions have led to improved public health or reduced damage to sensitive ecosystems.

14.1 Multipollutant Considerations

While current air quality regulations generally address single pollutants, most current control strategies take into account multipollutant interactions and have a multipollutant dimension. Thus, the capabilities for developing coordinated reductions in air pollution and implementing multipollutant air quality management at *Level 1* (and to some extent *Level 2*) currently exist. These capabilities are sufficiently mature and the ambient measurements and information about sources and emissions are sufficiently accurate to verify achievement of the existing goals or standards. These goals and standards, in turn, are established by comprehensive reviews of inferred single pollutant health and welfare effects on humans and ecosystems.

Moving toward a risk-based multipollutant management approach (*Levels 3 or 4*), however, requires developing multipollutant source control strategies that address “the most significant exposures [and] risks,” and result in “comprehensive reductions [in these risks or exposures] in the most cost-effective manner for all priority pollutants” (NRC 2004). Risk analysis frameworks exist that are suited, in principle, for analyzing alternative multipollutant management actions, given appropriate input information. Many elements of these frameworks, such as emission and air quality modeling, are already multipollutant in character. The principal missing features are the exposure and dose-response information that enables relative risk determination for exposure to single and multiple pollutants.

A first step in evolving to a formal risk-based multipollutant strategy (*Level 3*) would be to assess comparative risks on the basis of exposure to individual pollutants as indicators of complex mixtures derived from common sources. Alternative strategies would be considered for optimizing exposure reduction to pollutants that represent the highest population (or individual) risk, or the greatest net benefit for environmental protection, assuming that all risks are additive.

While we have information on the risks of exposure to individual criteria pollutants and some air toxics, this information contains significant uncertainties. These uncertainties include not only those associated with determining exposure, dose, and effect, but also, in some cases, uncertainties in whether the pollutant in question is the actual cause of an adverse effect or a surrogate for that effect. Although our knowledge may be sufficient for setting standards, these uncertainties are currently too great to allow a complete ranking of the severity of risk of exposure to individual pollutants. Partial rankings are feasible where there are large differences in the levels of exposure or toxicity and the agent causing the adverse effect is known unequivocally.

The next step in implementing a risk-based, multipollutant approach to air quality management (*Level 4*) would require a credible representative assessment of the effects of simultaneous exposure to multiple air pollutants.

Unfortunately, little is known about the human health and ecosystem effects of exposure to mixtures of pollutants other than to consider co-pollutants as confounders of the effects of the principal pollutant under consideration. Therefore, it is unlikely that this level of multipollutant air quality management could be implemented within the next five to ten years.

If a comprehensive multipollutant approach to air quality management is to be pursued, more attention will need to be given to the consequences and risks of multipollutant exposure. With respect to air toxics and human health, toxicological information could be used for relative risk assessment on the basis of potency (or reactivity) and exposure. However, little of this kind of relative risk assessment has been performed.

Investigators have had little incentive to study the toxic nature of pollutant mixtures except for studies of ecosystem effects, especially acidic deposition. Epidemiological methods have little power to address potential synergisms, but there is evidence from experimental exposures of biota in laboratory environments that some combinations of pollutants cause greater than additive effects. Although some additive and sub-additive effects have been demonstrated, current knowledge indicates that the potential for synergies cannot be ignored. With respect to ecosystems, there is some evidence that interactions between metals and acidity, as well as combinations of certain persistent organic pollutants, could have adverse synergistic effects in ecosystems.

The current practice for environmental protection is to specify and achieve ambient standards based on iterative evaluation of the literature on risks of exposure to *individual* pollutants, or the risk to individuals from exposure to *specific* toxic compounds. Alternatively, a strategy could be adopted that aims at reducing the most significant exposures—those presenting the greatest risks based on current knowledge for the greatest number of people.

With improved capabilities for characterizing exposure, air quality management actions could be prioritized according to which might be most effective in reducing exposure of broad population categories to the pollutants or

combinations of pollutants presenting the greatest risks as we currently understand them (and setting the stage for future accountability analysis and mid-course correction of management strategies).

This in essence is the goal of air quality management envisaged by the NRC (2004).

A further advance in multipollutant air quality management could be achieved through grouping of pollutants having similar sources, air chemistry or biological mechanisms of harm. Other approaches to dealing with the health effects of pollutant mixtures could also become available in the future. For example, the emerging field of computational toxicology (which involves the integrated application of genomics, proteomics, and advanced computational models) may offer fresh approaches to examining the toxicology of mixtures and assessing their effects.

Lastly, future multipollutant management could be complicated by three global-scale influences:

- Changes in precursor emissions, within North America as well as globally, that would result from actions taken to mitigate anthropogenic climate change.
- Changes in atmospheric chemistry, biogenic emissions, and meteorological conditions that could be brought about by climate change.
- Intra- and intercontinental transport of long-lived pollutants and pollutant precursors from increased global emissions, which could affect local and regional air quality management by increasing ambient background concentrations.

In principle, we have the observational and modeling tools needed to assess the effects of hemispheric transport on air quality. Also, modeling simulations indicate that climate change will not radically change our general approach to mitigating poor air quality, although climate change could affect the frequency and intensity of poor air quality episodes and increase the challenge of meeting air quality management goals. Perhaps the most dramatic effect of climate change on air quality, at least in the medium to longer term, could be the changes in emissions brought about by climate change and actions that might be taken to reduce it.

Addressing anthropogenic forcing of climate change through the reduction of greenhouse gas or particle emissions will require major changes in alternative energy and industrial resources, including transportation, electricity generation and end-use technology sectors. These changes, in turn, will likely have significant effects on air quality related emissions. These changes need to be taken in to account when projecting benefits of actions designed to address both air quality and climate related issues.

Based on our examination of the state-of-science, we recommend the following actions at high priority for furthering a transition from single-pollutant to a risk- and results-based multipollutant air quality management:

1. *Improve the ability to estimate pollutant exposure.*
   Improved knowledge of human exposure to known pollutants for a broad spectrum of microenvironments and exposure scenarios will sharpen our understanding of the effects of air pollution on human health and ecosystems. Achieving this goal will require measurement methods, monitoring strategies, and modeling

tools that support exposure assessment and the extrapolation of concentrations to exposure; account for outdoor conditions, indoor infiltration, and human activity patterns; and provide temporal and spatial resolution needed to represent the ambient concentration gradients associated with the pollution sources of concern. The data required will need to go beyond that needed to document ambient concentration patterns and trends of regulated pollutants, and include information on currently unregulated species, such as organonitrates and oxidants other than ozone, that are known or expected to pose health or environmental risks.

2. *Expand the focus of health and ecosystem effects research to include the effects of exposure to multiple pollutants and place increased emphasis on this problem*. Interdisciplinary research teams, including atmospheric, health and ecological scientists, should focus on four strategic questions: (a) What are the health and ecological damage burdens of air pollution in relationship to other environmental stressors? (b) Which pollutants and combinations of pollutants actually cause which effects, which pollutants dominate these effects, how do they interact, and how can we reduce uncertainty about the effects of exposure to single pollutants? (c) Is it feasible to group pollutants according to chemical structure or type, or some other feature, in order to expedite research on the effects of exposure to multiple pollutants? (d) Can we construct objective metrics for prioritizing health versus ecosystem effects? The emphasis in addressing these questions should be to improve our understanding of the risks of exposure to pollutant mixtures and of the relative risks of exposure to individual pollutants.
3. *Improve emission information and emission control technologies*.
   Multipollutant emission characterization would include (a) implementation of recommendations of the NARSTO (2005) Emission Inventory Assessment, (b) improving communication between the health effects and emissions information development communities to ensure that emissions inventories include, to the extent feasible, all substances thought to pose risks to human health and ecosystems, (c) expanding the range of substances and sources that can be measured directly, and (d) encouraging the development of multipollutant emission control technologies that could reduce the cost and improve the effectiveness of emission reduction programs.
4. *Modify the designs of air quality measurement programs to enhance support for multipollutant air quality management.*
   The present air monitoring programs in North America satisfy the needs for compliance monitoring and some multipollutant surveillance. However, within current or declining resources, opportunities to shift resources to improve multipollutant measurements exist. Such improvements include: (a) expanding coverage for speciated VOCs and particulate organic tracer compounds, (b) expanding the measurement capabilities of current monitoring systems by using advanced instrumentation already proven to be reliable, (c) coordinating current measurement objectives with those needed to support epidemiological studies, including provision for at least occasional intermittent sampling in areas of strong concentration gradients (e.g. roadway zones), and (d) conducting special campaigns to measure exposure-related parameters and non-regulated species including oxidants, a wider range of reactive nitrogen species, and ammonia. In Canada, one

or two additional multipollutant sites are needed in the northern tier to establish better coverage of remote regions. In Mexico, expanded and sustained measurements in cities other than Mexico City are needed, adding two regionally representative multipollutant sites in rural, central or northern Mexico to characterize pollution on a larger scale.

5. *Undertake one or more pilot studies of the feasibility of implementing a risk-based, results-oriented multipollutant approach to air quality management.* Feasibility studies are needed to extend integrated regulatory studies such as those reported for Detroit, Atlanta and the Los Angeles area. The assertion of NRC (2004) that multipollutant approaches at *Level 2* and higher would improve the effectiveness and efficiency of air quality management needs to be tested for both criteria pollutants and air toxics. In addition, trend and retrospective studies are needed to evaluate the fidelity of "weight of evidence" projections used for achieving goals to assess the reliability of such projections. Particular attention should be given to developing and enhancing methods for establishing exposure and multipollutant effects pathways for human and (vulnerable) ecosystems. These studies also could be integrated into accountability procedures, as outlined in Fig. 3.2.
6. *Analyze the potential effects of technological change, especially those changes related to climate change, on future air quality and its effects on human health and ecosystems.* New fuels or changes in primary energy production or end-use technologies introduced to constrain climate forcing potentially will affect air quality management. Current methods for projecting future air quality adjust emission inventories for socio-economic growth expected for incremental changes in status quo of the energy production and transportation sectors. These adjustments are adopted for planning models to meet air quality goals. Within less than the next few decades, major, accelerated changes in technological infrastructure are likely to take place. The direction and extent of these changes need to be imbedded as scenarios in current emissions models. In this way, a range of future air quality scenarios can be estimated to determine the robustness of the management strategies for North America. Since climate change may change the current estimates of natural emissions, evaluation of scenarios addressing PM_x, VOCs including methane, and nitrogen compounds also should be considered along with selected HAPs.

14.2 Accountability Considerations

As accountability is exploited further for evaluating and adjusting air quality management actions, it will become integral to air quality planning and rulemaking. If adopted, the design of a scientifically credible accountability program within a multipollutant framework should be a required component of new or on-going air quality management actions. Careful design is critical to demonstrating the linkages in the accountability chain from emissions to health and ecological effects. A meaningful accountability program would need to demonstrate that the accountability measures could be determined to some reasonable level of statistical certainty to be credible to stakeholders.

No formal, complete retrospective analysis, through the accountability chain described in Fig. 3.2, has been performed on a specific air quality management action to determine whether the expected results of the action was achieved in practice.

Considerable "weight-of-evidence" from measurements and modeling indicates that past air quality management actions have improved air quality (i.e., reduced ambient concentrations with estimated reductions in emissions) for criteria pollutants and air toxics. Emerging evidence indicates that actions taken to reduce ambient concentrations of particulate matter evidently have reduced adverse health effects associated with exposure to PM_x ambient concentrations. For ozone, reductions in maximum concentrations have been reported in many locations. The resulting improvement in human health has been inferred from a range of studies, including anecdotal information from affected areas. In the case of ecosystems, terrestrial systems exposed to ozone or acid gas exposure at high concentrations take many years to recover. However, reductions in emissions of acid-forming substances, especially SO_2, have been linked to reductions in acidic deposition and improvements in surface aquatic systems, although biota recovery remains problematic.

Uncertainties in, and in some cases the lack of information on, emissions associated with adverse health and ecosystem outcomes remain an important barrier to implementation of formal accountability procedures.

Characterizing and verifying post-1990s changes in emissions from sources equipped with continuous emission measurement (CEM) systems is relatively straightforward. However, it is much more difficult to verify changes in mobile, complex industrial, small point, and area sources. These classes of sources are estimated using emission models, which vary in their quality and reliability. Speciated emission data for VOCs and particle composition, in particular, are limited and of uncertain quality. These elements are essential for applying accountability by tracing emissions of specific compounds through ambient concentrations to their potential effects.

Given reasonably accurate emission information, it is feasible to determine whether or not specific management actions for addressing criteria pollutants (or their equivalents in Canada and Mexico) have had their intended effect in reducing ambient concentrations, improving visibility, or decreasing deposition of potentially injurious substances to sensitive ecosystems. Although we have the measurement and modeling capabilities for executing this level of accountability, the analysis of results from existing monitoring networks in North America have not provided complete information needed for reliable, quantitative verification.

As a major component of management strategies, we strongly recommend a formal, quantitative demonstration that mandated emission reductions have been achieved along with a demonstration of the expected changes in ambient concentrations or deposition.

Difficulties in determining quantitatively whether or not differences between predicted and observed changes in ambient air quality or deposition are due to errors in ambient measurements, errors in emissions information, errors or deficiencies in understanding or representation of relevant atmospheric processes in air quality models used, the uncertainties of predicted versus actual meteorology, or in the way the models were implemented (or all of the above) should not be under estimated. Scientists have recognized these issues for some time and consequently have worked on their resolution. There is sufficient knowledge about all of these issues to estimate probability distributions of outcomes and incorporate error estimates in the comparisons between projections and observations.

Demonstrating that specific air quality management actions have resulted in improvements in human health (or ecosystem function) is extremely difficult to achieve. Time series demonstrations require air quality and health related measurements over long periods (greater than ten years) to differentiate the signal of reduced mortality or morbidity due to changes in pollution exposure from the "noise" associated with confounding factors.

Until recently, analyses of changes on human health measures with changes in ambient pollutant concentrations have yielded very limited accountability related results. Intervention or natural experiments in which the influence of sudden specific emission reductions from specific sources on public health indicators have provided important evidence of local health improvement accompanying reductions in pollution. Moreover, recent reports on time series analyses of the health consequences of gradual reductions in particulate pollution indicate opportunities for establishing accountability relationships. Such opportunities are reinforced by knowledge of the apparent toxicity of effluents from certain sources or their atmospheric end products at ambient concentrations, using weight-of-evidence arguments including receptor modeling. These studies provide important caveats about the assumptions applied in the analyses and the reliability of measures taken to minimize the influence of confounders. Even so, with improving long term air quality data records and health records, the recent studies show that there are major opportunities to demonstrate that reductions in pollution can be related to improvements in public health. The approaches used in these recent studies provide guidance for moving toward *Level 3* and *4* management options.

Biomarkers are useful indicators for relating air quality changes to change in human health. The use of biomarkers is relatively straightforward for primary pollutants, such as lead or mercury in the bloodstream. For pollutants having a lack of specific identified or reliable biomarkers (e.g., oxidants or particle components), changes in public health with changes in air quality relies on using a combination of ambient and epidemiological inference, combined with exposure modeling.

Application ambient data and biomarkers have proven to be useful as indexes for pollutant exposure, and interpretation of health outcomes. Expansion of this approach offers an opportunity to find practical means of establishing relationships between pollutants or groups of pollutants having a common and identifiable toxicological impact. If additional biomarkers could be identified and exploited, linkages between changes in pollutant concentrations, de-facto exposure, and an index for response could be used for accountability demonstrations in direct analogy to the results for lead and mercury.

Accountability for effects of air pollution exposure from deposition to vulnerable ecosystems has advanced in similar ways to that human health effects, especially for acidification of aquatic systems. Changes in terrestrial ecosystems with pollution reductions have been difficult to verify not only for acidic deposition, but also for oxidants, trace metals, and persistent organic pollutants.

Changes in chemistry of vulnerable surface waters from reduction in sulfur oxide emissions and sulfate deposition have been documented semi-quantitatively in accordance with expectations of emission reductions in eastern North America. However, the recovery of biota has been far slower than the response in water chemistry. Research to date has shown the difficulty of attributing changes in managed or unmanaged terrestrial ecosystems systems to reductions in exposure to contemporary levels of air pollution (including acids, acid gases, oxidants, metals or persistent organic pollutants) for reasons similar to those found for humans. Additional support for long-term surveillance of representative ecological sites would assist the verification of expected changes in relation to pollution exposure, not only in water and soils chemistry, but also in biological changes involving species survival and diversity.

Based on our examination of the state-of-science, we recommend the following actions at high priority for improving our ability to demonstrate accountability:

1. *Two or more retroactive test cases should be undertaken to demonstrate the current capability for determining full accountability for past major air quality programs or rules.*
   These test cases should bring together the best available information in a formal assessment down the accountability chain and serve as a starting place for future accountability improvement. As the first step in implementing this recommendation, we strongly recommend that the ability to achieve at least Step 2 of the accountability chain be explored before accountability is mandated as a component of future air quality management decisions.
   In Mexico, the principal source of data to establish trends in ambient air quality for criteria pollutants is in the Valley of Mexico (Mexico City). To facilitate the establishment of broader accountability in Mexico, we recommend that development of their national monitoring network be pursued as rapidly as practical. Further, there is a need in Mexico for a sustained survey of air toxics in urban areas beyond currently conducted in Mexico City.
2. *Verify and improve emission estimates from model-estimated source categories.*
   Characterizing and verifying changes in emissions from sources equipped with continuous emissions measurement systems are relatively simple. However, it is much more difficult for the large number of mobile, complex industrial, small point-sources, and area-sources for which emissions must be estimated by means of emission models. Uncertainties in, and in some cases the lack of information on, emissions responsible for adverse health and ecosystem outcomes

remains a fundamental barrier to implementation of formal accountability procedures. Model verification and improvements must include better speciation information that encompasses, to the extent possible, all substances known or suspected to adversely affect human health or ecosystems. Specific examples include:

- Improving onroad and nonroad mobile source emission models by measuring exhaust and evaporative emissions from statistically representative samples of in-use vehicles or equipment for a representative range of environmental conditions and operating modes. Improved characterization of volatile organic compounds, semivolatile organic compounds, and carbon particulate emissions are of particular interest. The use of micro-sensors for continuously measuring oxides of nitrogen, carbon monoxide, volatile organic compound emissions coordinated with measurements of carbon dioxide or fuel consumption would be a valuable innovation.
- Improving estimates of ammonia emissions from agricultural sources and verifying these models for the range of climatic conditions, agricultural economies, and agricultural practices across North America.
- Instituting focused research and development programs for characterizing emissions and improving emission estimates for strategically important source categories (including wildfires, windblown dust, road dust, and air toxics), which will vary by country and by region.
- Increasing information exchange between the health effects and emissions characterization communities to ensure that emissions thought to pose the greatest health-risk potential are measured or modeled accurately over a range of space and time scales. Such emissions information may include substances not included in traditional emissions inventories.
- Maintaining continuity and comparability in a time-continuous record of emissions inventories to enable retrospective analyses of past air quality management actions. Particular emphasis needs to be placed on documenting changes in emissions developed from models that are frequently updated to incorporate methodology improvements. Not having this information hampers the ability to compare results over time.

An important priority for Mexico should be to undertake an assessment of the adequacy of current emission inventories for supporting an accountability assessment of the effectiveness of current air quality management actions in reducing concentrations of ambient pollutants. This demonstration could focus initially on the effects of reducing sulfur concentrations in transportation-sector fuels.

Consideration should also be given to increasing, where practical, the number of large point sources in North America equipped with continuous emission monitoring systems. Furthermore, we recommend that a significant level of funding be provided, through mechanisms such as the U.S. Small Business Innovation Research program, for the development of small, potentially low-cost, emission measurement systems that would increase the number of source categories that could be measured directly either on an operational basis or for improving the accuracy of emission models.

3. *Identify reliable biomarkers of exposure for a larger number of air pollutants.*
   Air quality goals for criteria air pollutants are generally expressed in terms of ambient concentrations, and it is assumed that attainment of these goals will be reasonably protective of human health. However, knowing broad-scale average ambient concentrations is often insufficient for determining human exposure and, eventually, dose. First, for many pollutants current ambient monitoring and air quality modeling do not supply information on the spatial and temporal scales relevant to actual individual exposures. Second, ambient concentrations of pollutants associated with many sources of concern, such as high traffic-density roadways or toxic air pollutant "hot spots," may vary sharply with distance from the source, with season, or with time of day. Third, estimating exposure to pollutants of ambient origin requires knowledge of how and for how long affected individuals move through this concentration space, what they are doing while they are there, the infiltration of ambient pollutants into indoor environments occupied by affected individuals, as well as other factors.
4. *Rethink current monitoring network design and sampling strategies and focus their mission on providing the information needed for improved exposure assessment. Continue the development of improved exposure assessment models and methodologies for exploiting exposure-focused observations.*
   For pollutants having no practical biomarkers, exposure must be estimated using a combination of measurements and modeling tools. Measurements and modeling tools may also be needed to supplement the information deduced from biomarkers. If the ambient concentrations of the pollutant or pollutants in question are relatively homogeneous in space and time, assessing the impact of air quality actions on exposure is relatively straightforward. Estimating exposure for pollutants presenting significant spatial and temporal variability, however, will require improvements in exposure modeling procedures and monitoring network design. Given sufficient investments, we believe that significant improvements in exposure information are possible within the near future (i.e., five to ten years).
   The spatial and temporal detail required for exposure assessment cannot be generated by monitoring alone. Exposure characterization will require a more nuanced approach that combines long-term monitoring measurements with modeling and intensive diagnostic measurement campaigns that provide practical estimates of the appropriate ambient concentrations. These estimates, combined with improved exposure models, can then be used to provide estimates of individual exposures (as needed for some air toxics), or population exposures (as needed for some criteria air pollutants). Development of approaches for providing the kinds of detailed ambient concentration fields needed for exposure assessment will require implementation of a number of field studies in several venues across North America in order to test and evaluate the new methods, monitoring network designs, sampling strategies, and data analysis procedures that would be required to take accountability to this level of detail.

5. *If complete accountability is adopted as a tool for evaluating and adjusting air quality management actions, it must become an integral part of the air quality planning and rulemaking process.*
   A technically credible accountability program would demonstrate the linkages in the accountability chain from emissions to exposure; it would demonstrate that the accountability metrics can be determined to some reasonable level of statistical uncertainty; and it would need to be adequately funded.

14.3 Concluding Remarks

This NARSTO assessment concludes that a multipollutant approach to air quality management is currently feasible through *Level 2* as described in Chap. 3, and that coordination of air quality management actions at this level could have considerable management benefit. The assessment also concludes that given sufficiently accurate emission information, accountability through accountability step 2 in Chap. 3 (verification that the air quality management action in question has achieved the expected reductions in ambient concentrations or deposition) is feasible and could provide valuable information for assessing or improving air quality management actions. However, it is recommended that this conclusion be well tested before this level of accountability is made a formal part of the design and implementation of air quality management systems.

Moving to more advanced levels of multipollutant air quality management and accountability as envisaged by hypothetical *Levels 3* and *4* is problematic, at least in the near term. National priorities for resources available for environmental protection are likely to continue to be limited, even for the present programs. To go well beyond these programs by addressing *Level 3* and *4* options will require substantial additional stakeholder investment, as well potential changes in administrative policies. An exception could be increased emphasis on a multipollutant approach for exposure evaluation. Improved exposure characterization combined with current knowledge of toxicity would allow decision-makers to prioritize actions according to those deemed to be most effective in reducing exposure to pollutants or combinations of pollutants presenting the greatest risks as we currently understand them.

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