

Acid Rain - Deposition to Recovery

Acid Rain - Deposition to Recovery

Edited by

PETER BRIMBLECOMBE
*University of East Anglia,
Norwich, UK*

HIROSHI HARA
*Tokyo University of Agriculture and Technology,
Tokyo, Japan*

DANIEL HOULE
*Saint-Lawrence Centre, Montreal, Environment Canada;
Forest Division, Quebec Ministry of Natural Resources and Wildlife,
Quebec, Canada*

and

MARTIN NOVAK
*Czech Geological Survey,
Prague, Czech Republic*

Reprinted from *Water, Air, & Soil Pollution: Focus*, Volume 7, Issues 1-3, 2007

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN:978-1-4020-5884-4 (HB)
ISBN:978-1-4020-5885-1 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

Cover image: Frozen Trnavka River by Tomáš Paces (reproduced with permission)

All Rights Reserved

© 2007 Springer

No part of this work may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission from the Publisher, with the exception of any material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work.

TABLE OF CONTENTS

P. BRIMBLECOMBE / Preface	1–2
S. HELLSTEN, U. DRAGOSITS, C. J. PLACE, T. H. MISSELBROOK, Y. S. TANG and M. A. SUTTON / Modelling Seasonal Dynamics from Temporal Variation in Agricultural Practices in the UK Ammonia Emission Inventory	3–13
CAMILLA ANDERSSON and JOAKIM LANGNER / Inter-annual Variations of Ozone and Nitrogen Dioxide Over Europe During 1958–2003 Simulated with a Regional CTM	15–23
WENCHE AAS, JAN SCHAUG and JAN ERIK HANSEN / Field Intercomparison of Main Components in Air in EMEP	25–31
BARBARA WALNA, IWONA KURZYCA and JERZY SIEPAK / Variations in the Fluoride Level in Precipitation in a Region of Human Impact	33–40
DAVID FOWLER, ROGNVALD SMITH, JENNIFER MULLER, JOHN NEIL CAPE, MARK SUTTON, JAN WILLEM ERISMAN and HILDE FAGERLI / Long Term Trends in Sulphur and Nitrogen Deposition in Europe and the Cause of Non- linearities	41–47
PIERRE SICARD, PATRICE CODDEVILLE, STÉPHANE SAUVAGE and JEAN-CLAUDE GALLOO / Trends in Chemical Composition of Wet-only Precipitation at Rural French Monitoring Stations Over the 1990–2003 Period	49–58
CHRISTOPHER M. B. LEHMANN, VAN C. BOWERSOX, ROBERT S. LARSON and SUSAN M. LARSON / Monitoring Long-term Trends in Sulfate and Ammonium in US Precipitation: Results from the National Atmospheric Deposition Program / National Trends Network	59–66
IZUMI NOGUCHI, KENTARO HAYASHI, MASAHIDE AIKAWA, TSUYOSHI OHIZUMI, YUKIYA MINAMI, MORITSUGU KITAMURA, AKIRA TAKAHASHI, HIROSHI TANIMOTO, KAZUhide MATSUDA and HIROSHI HARA / Temporal Trends of Non-sea Salt Sulfate and Nitrate in Wet Deposition in Japan	67–75
E. TERAUDA and O. NIKODEMUS / Sulphate and Nitrate in Precipitation and Soil Water in Pine Forests in Latvia	77–84
MARCOS A. DOS SANTOS, CYNTHIA F. ILLANES, ADALGIZA FORNARO and JAIR J. PEDROTTI / Acid Rain in Downtown São Paulo City, Brazil	85–92
STEPHEN A. NORTON / Atmospheric Metal Pollutants-Archives, Methods, and History	93–98
BRIDGET A. EMMETT / Nitrogen Saturation of Terrestrial Ecosystems: Some Recent Findings and Their Implications for Our Conceptual Framework	99–109
B. J. HAWORTH, M. R. ASHMORE and A. D. HEADLEY / Effects of Nitrogen Deposition on Bryophyte Species Composition of Calcareous Grasslands	111–117

KENTARO HAYASHI, MICHIO KOMADA and AKIRA MIYATA / Atmospheric Deposition of Reactive Nitrogen on Turf Grassland in Central Japan: Comparison of the Contribution of Wet and Dry Deposition	119–129
MASAHIRO YAMAGUCHI, MAKOTO WATANABE, NAOKI MATSUO, JUNICHI NABA, RYO FUNADA, MOTOHIRO FUKAMI, HIDEYUKI MATSUMURA, YOSHIHISA KOHNO and TAKESHI IZUTA / Effects of Nitrogen Supply on the Sensitivity to O ₃ of Growth and Photosynthesis of Japanese Beech (<i>Fagus crenata</i>) Seedlings	131–136
ULF SIKSTRÖM / Stem Growth of <i>Picea Abies</i> in South Western Sweden in the 10 Years Following Liming and Addition of PK and N	137–142
ALLAN G. SANGSTER, LEWIS LING, FRÉDÉRIC GÉRARD and MARTIN J. HODSON / X-ray Microanalysis of Needles from Douglas Fir Growing in Environments of Contrasting Acidity	143–149
BOHAN LIAO, ZHAOHUI GUO, QINGRU ZENG, ANNE PROBST and JEAN-LUC PROBST / Effects of Acid Rain on Competitive Releases of Cd, Cu, and Zn from Two Natural Soils and Two Contaminated Soils in Hunan, China	151–161
HARALD SVERDRUP, SALIM BELYAZID, BENGT NIHLGÅRD and LARS ERICSON / Modelling Change in Ground Vegetation Response to Acid and Nitrogen Pollution, Climate Change and Forest Management at in Sweden 1500–2100 A.D.	163–179
ATSUYUKI SORIMACHI and KAZUHIKO SAKAMOTO / Laboratory Measurement of Dry Deposition of Ozone onto Northern Chinese Soil Samples	181–186
MILOŠ ZAPLETAL and PETR CHROUST / Ozone Deposition to a Coniferous and Deciduous Forest in the Czech Republic	187–200
CECILIA AKSELSSON, OLLE WESTLING, HARALD SVERDRUP, JOHAN HOLMQVIST, GUNNAR THELIN, EVA UGGLA and GUNNAR MALM / Impact of Harvest Intensity on Long-Term Base Cation Budgets in Swedish Forest Soils	201–210
WENDELIN WEIS, ROLAND BAIER, CHRISTIAN HUBER and AXEL GÖTTLEIN / Long Term Effects of Acid Irrigation at the Höglwald on Seepage Water Chemistry and Nutrient Cycling	211–223
JOHAN BERGHOLM, HOOSHANG MAJDI and TRYGGVE PERSSON / Nitrogen Budget of a Spruce Forest Ecosystem After Six-year Addition of Ammonium Sulphate in Southwest Sweden	225–234
J. C. NÓVOA-MUÑOZ and E. GARCÍA-RODEJA GAYOSO / Modification of Soil Solid Aluminium Phases During an Extreme Experimental Acidification of A Horizons of Forest Soils from Southwest Europe	235–239
JOHAN TIDBLAD, VLADIMIR KUCERA, FARID SAMIE, SURENDRA N. DAS, CHALOTHORN BHAMORNSUT, LEONG CHOW PENG, KING LUNG SO, ZHAO DAWEI, LE THI HONG LIEN, HANS SCHOLLENBERGER, CHOZI V. LUNGU and DAVID SIMBI / Exposure Programme on Atmospheric Corrosion Effects of Acidifying Pollutants in Tropical and Subtropical Climates	241–247

- VLADIMIR KUCERA, JOHAN TIDBLAD, KATERINA KREISLOVA, DAGMAR KNOTKOVA, MARKUS FALLER, DANIEL REISS, ROLF SNETHLAGE, TIM YATES, JAN HENRIKSEN, MANFRED SCHREINER, MICHAEL MELCHER, MARTIN FERM, ROGER-ALEXANDRE LEFÈVRE and JOANNA KOBUS / UN/ECE ICP Materials Dose-response Functions for the Multi-pollutant Situation 249–258
- T. YAMADA, T. INOUE, H. FUKUHARA, O. NAKAHARA, T. IZUTA, R. SUDA, M. TAKAHASHI, H. SASE, A. TAKAHASHI, H. KOBAYASHI, T. OHIZUMI and T. HAKAMATA / Long-term Trends in Surface Water Quality of Five Lakes in Japan 259–266
- MARY BETH ADAMS, JAMES N. KOCHENDERFER and PAMELA J. EDWARDS / The Fernow Watershed Acidification Study: Ecosystem Acidification, Nitrogen Saturation and Base Cation Leaching 267–273
- ANDREAS MEYBOHM and KAI-UWE ULRICH / Response of Drinking-water Reservoir Ecosystems to Decreased Acidic Atmospheric Deposition in SE Germany: Signs of Biological Recovery 275–284
- BJØRN MEJDELL LARSEN, ODD TERJE SANDLUND, HANS MACK BERGER and TRYGVE HESTHAGEN / Invasives, Introductions and Acidification: The Dynamics of a Stressed River Fish Community 285–291
- ARNE FJELLHEIM, ÅSMUND TYSSE and VILHELM BJERKNES / Fish Stomachs as a Biomonitoring Tool in Studies of Invertebrate Recovery 293–300
- SHAUN A. WATMOUGH, JULIAN AHERNE, M. CATHERINE EIMERS and PETER J. DILLON / Acidification at Plastic Lake, Ontario: Has 20 Years Made a Difference? 301–306
- DAVID MONCOULON, ANNE PROBST and LIISA MARTINSON / Modeling Acidification Recovery on Threatened Ecosystems: Application to the Evaluation of the Gothenburg Protocol in France 307–316
- W. KELLER, N. D. YAN and J. M. GUNN J. HENEBERRY / Recovery of Acidified Lakes: Lessons From Sudbury, Ontario, Canada 317–322
- RICHARD K. JOHNSON, WILLEM GOEDKOOP, JENS FÖLSTER and ANDERS WILANDER / Relationships Between Macroinvertebrate Assemblages of Stony Littoral Habitats and Water Chemistry Variables Indicative of Acid-stress 323–330
- JENS FÖLSTER, CECILIA ANDRÉN, KEVIN BISHOP, ISHI BUFFAM, NEIL CORY, WILLEM GOEDKOOP, KERSTIN HOLMGREN, RICHARD JOHNSON, HJALMAR LAUDON and ANDERS WILANDER / A Novel Environmental Quality Criterion for Acidification in Swedish Lakes – An Application of Studies on the Relationship Between Biota and Water Chemistry 331–338

VIII

- TRYGVE HESTHAGEN, BJØRN WALSING, LEIF ROGER KARLSEN and ROY M. LANGÅKER / Effects of Liming on the Aquatic Fauna in a Norwegian Watershed: Why Do Crustaceans and Fish Respond Differently? 339–345
- OLLE WESTLING and THERESE ZETTERBERG / Recovery of Acidified Streams in Forests Treated by Total Catchment Liming 347–356
- KEN YAMASHITA, FUMIKO ITO, KEIGO KAMEDA, TRACEY HOLLOWAY and MATTHEW P. JOHNSTON / Cost-effectiveness Analysis of Reducing the Emission of Nitrogen Oxides in Asia 357–369
- J. SLOOTWEG, J.-P. HETTELINGH, M. POSCH, G. SCHÜTZE, T. SPRANGER, W. DE VRIES, G. J. REINDS, M. VAN 'T ZELFDE, S. DUTCHAK, and I. ILYIN / European Critical Loads of Cadmium, Lead and Mercury and their Exceedances 371–377
- J.-P. HETTELINGH, M. POSCH, J. SLOOTWEG, G. J. REINDS, T. SPRANGER and L. TARRASON / Critical Loads and Dynamic Modelling to Assess European Areas at Risk of Acidification and Eutrophication 379–384
- MATTIAS ALVETEG and LIISA MARTINSON / On the Calculation and Interpretation of Target Load Functions 385–390
- LIZ HEYWOOD, RICHARD SKEFFINGTON, PAUL WHITEHEAD and BRIAN REYNOLDS / Comparison of Critical Load Exceedance and Its Uncertainty Based on National and Site-specific Data 391–397
- RICHARD A. WADSWORTH and JANE R. HALL / Setting Site Specific Critical Loads: An Approach using Endorsement Theory and Dempster–Shafer 399–405
- MALCOLM S. CRESSER / Why Critical Loads of Acidity and N for Soils Should be Based on Pollutant Effective Concentrations Rather Than Deposition Fluxes 407–412
- JANE HALL, JACKIE ULLYETT, RICHARD WADSWORTH and BRIAN REYNOLDS / The Applicability of National Critical Loads Data in Assessing Designated Sites 413–419

Preface

P. Brimblecombe

Received: 14 November 2006 / Accepted: 28 November 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Acid rain is still with us. Yet it no longer evokes the wide public interest it did in the 1980s and increasingly seems relegated to outdated school text books. In reality the focus of acid rain research has shifted and it was these changes that were particularly evident at the Acid Rain 2005 conference, which took place in the Prague Congress Centre from 12 to 17th June, 2005. This was the seventh conference in a series that stretches back to the founding meeting in Columbus Ohio, in 1975. Although papers presented at the conference treated such traditional topics as emissions, precipitation composition and deposition, there was a wide range of other topics that illustrated the widening perspective we take on acid rain. These included much new material on ecosystem loads and recovery. The role of nutrients, particularly nitrogen, received greater emphasis than in the past. There was also a larger interest in metals in ecosystems and a move to bring more attention to health considerations.

There were more than 20 sessions covering a broad range of topics: (1) Emissions and their control. (2) Long-range transport and its modelling. (3) Atmospheric and deposition processes. (4) Acidification and persistent organic compounds. (5) Air pollution and

effects of non-acidic pollutants (ozone and particles). (6) Acidification outside Europe and North America. (7) Soil acidification and recovery; nutrient imbalances. (8) Forest damage. (9) Biogeochemical cycles. (10) Water acidification. (11) Effects on aquatic biota. (12) Role of organic carbon in ecosystem acidification. (13) Modelling of acidification processes and trends. (14) Critical loads. (15) Mitigation of soil and water acidification. (16) Long-term trends of acidification and recovery – regional case studies (17) Acidification and global change. (18) Acidification and metals. (19) Ecosystem experiments. (20) Nitrogen effects on ecosystems. (21) Archives of historic data. (22) Air pollution and its effect on materials and cultural heritage. (23–24) Regional and hemispheric. (25) Health effects of air pollution.

Invited plenary lectures at Acid Rain 2005 included: 1. Charles T. Driscoll, Syracuse University, USA – Effects of the acidic deposition on aquatic ecosystems. 2. Henning Rodhe, Stockholm University, Sweden – History and present of the acid rain research. 3. Bridgett Emmett, Centre for Ecology and Hydrology, Bangor, UK – Acid deposition and the nitrogen cycle. 4. Roland Psenner, University of Innsbruck, Austria – Global change and acid rain. 5. Jakub Hruska, Czech Geological Survey, Czech Republic – Effects of the acidic deposition on terrestrial ecosystems. 6. Stephen A. Norton, University of Maine, USA – Pollution by non-acidic pollutants and their linkage with acidifica-

P. Brimblecombe (✉)
School of Environmental Sciences,
University of East Anglia,
Norwich NR4 7TJ, UK
e-mail: P.Brimblecombe@uea.ac.uk

tion effects. 7. Keith Bull, United Nations, Switzerland – Interface between the science of acid rain and policy.

Close to six hundred participants from more than thirty countries gathered for this key event in Prague. The location was particularly symbolic given the high sulphur deposition in the region in the 20th century, which had such a great impact on forest ecosystems and materials. The conference in the Czech Republic not only reminded us of a recent reduction in the effects of pollutants, but also allowed us to undertake field trips to forests, coal mines, power-plants and test sites where so much work related to acid rain had been done.

This volume represents just a selection of the work of the conference and cannot do justice to the quantity and variety of excellent material. The initial selection committee of Martin Novak, Hiroshi Hara and Peter Brimblecombe met at the conference and tried to incorporate a range of papers that would reflect the style of the conference. These are being published in *Water, Air, & Soil Pollution: Focus* and *Applied*

Geochemistry. The volume here emphasises a number of themes: the emission, concentration and deposition of pollutants; nitrogen and trace elements in ecosystems and their effects on forests, water and soil; studies of material damage, ecosystem recovery and critical loads.

As with all conferences one is aware of the enormous effort involved. Here we were grateful for the work done by the organising committee chaired by Jaroslav Šantroch of the Czech Hydrometeorological Institute and the Executive Committee chaired by Jakub Hruška of the Czech Geological Survey. The International Scientific Committee chaired by Bedřich Moldan of Charles University of the Czech Republic was influential in meeting early in the planning stage to structure the topics that formed the basis of the program.

The geographical shift in the acid rain problem was also seen from the presence of so many scientists from China and the Asia – Pacific rim. Acid rain here shows itself in novel ways and it is particularly significant that China will host Acid Rain 2010.

Modelling Seasonal Dynamics from Temporal Variation in Agricultural Practices in the UK Ammonia Emission Inventory

S. Hellsten · U. Dragosits · C. J. Place ·
T. H. Misselbrook · Y. S. Tang · M. A. Sutton

Received: 17 June 2005 / Revised: 16 February 2006 / Accepted: 12 March 2006 / Published online: 6 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Most ammonia (NH_3) emission inventories have been calculated on an annual basis and do not take into account the seasonal variability of emissions that occur as a consequence of climate and agricultural practices that change throughout the year. When used as input to atmospheric transport models to simulate concentration fields, these models therefore fail to capture seasonal variations in ammonia concentration and dry and wet deposition. In this study, seasonal NH_3 emissions from agriculture were modelled on a monthly basis for the year 2000, by incorporating temporal aspects of farming practice. These monthly emissions were then spatially distributed using the AENEID model (Atmospheric Emissions for National Environmental Impacts Determination). The monthly model took the temporal variation in the magnitude

of the ammonia emissions, as well as the fine scale (1-km) spatial variation of those temporal changes into account to provide improved outputs at 5-km resolution. The resulting NH_3 emission maps showed a strong seasonal emission pattern, with the highest emissions during springtime (March and April) and the lowest emissions during summer (May to July). This emission pattern was mainly influenced by whether cattle were outside grazing or housed and by the application of manures and fertilizers to the land. When the modelled emissions were compared with measured NH_3 concentrations, the comparison suggested that the modelled emission trend corresponds fairly well with the seasonal trend in the measurements. The remaining discrepancies point to the need to develop functional parametrisations of the interactions with climatic seasonal variation.

S. Hellsten · U. Dragosits · Y. S. Tang · M. A. Sutton
Centre for Ecology and Hydrology Edinburgh, Bush Estate,
Edinburgh, Scotland EH26 0QB, UK

S. Hellsten · U. Dragosits · C. J. Place
Institute of Geography, The University of Edinburgh,
Drummond Street, Edinburgh EH8 9XP, UK

S. Hellsten (✉)
IVL Swedish Environmental Research Institute Ltd,
P.O. Box 5302, 400 14 Gothenburg, Sweden
e-mail: sofie.hellsten@ivl.se

T. H. Misselbrook
Institute of Grassland and Environmental Research,
North Wyke, Okehampton, Exeter EX 2SB, UK

Keywords ammonia emissions · GIS · modelling ·
seasonal dynamics · temporal resolution

1 Introduction

Long-term measurements of ammonia (NH_3) concentrations have shown that seasonal variations in concentrations occur during the year (Horvath & Sutton, 1998; Huber & Kreutzer, 2002; Sutton et al., 2001; Tang & Sutton, 2004; Yamamoto, Nishiura, Honjo, Ishikawa, & Suzuki, 1995). These variations are associated with both climatic conditions (mainly temperature) and farming activity (such as manure

application). Generally, ammonia emission inventories have been calculated on an annual basis, therefore failing to capture these seasonal variations in emissions. When these data are applied as input in atmospheric transport models to assess environmental impacts, these emission results will only provide the average impact, and therefore fail to capture seasonal patterns that may occur during the year.

In the UK, the AENEID model (Atmospheric Emissions for National Environmental Impacts Determination model) has been developed to calculate the spatial distribution of NH_3 emissions (Dragosits, Sutton, Place, & Bayley, 1998). Firstly, the model spatially distributes the emission source types (e.g. animal housing and manure spreading activities from parish aggregated Agricultural Census Data) across the landscape, onto suitable land types derived from satellite land cover data (Fuller, Smith, Sanderson, Hill, & Thomson, 2002), and secondly, the model assigns emission potentials ('emission factors') to these sources. Emissions are modelled at a 1-km grid resolution, but generalized to 5-km resolution for mapping. The AENEID model is used to spatially distribute ammonia emissions in the UK National Atmospheric Emission Inventory (NAEI), and is also used as a component model for the UK National Ammonia Reduction Strategy Evaluation System (NARSES).

2 Materials and Methods

For the purpose of calculating seasonal NH_3 emissions, temporal activity data for agricultural source activities (livestock grazing and/or housing, manure storage and manure application) were dis-aggregated into a monthly temporal resolution (see Table 1). This work represented an extension to the agricultural atmospheric emission inventory of ammonia emissions in the UK (IAEUK) (Misselbrook et al., 2000, 2003). IAEUK calculates annual NH_3 emissions using emission factors for each livestock class for each of the various manure management stages (livestock housing, manure storage, manure spreading and grazing). For instance, the UK emission from dairy cows during housing in cubicles each year is derived from activity data (number of dairy cows in the UK, percentage of dairy cows kept in cubicle houses and number of days per year spent housing) and an emission factor (e.g. $\text{g NH}_3\text{-N (livestock unit)}^{-1} \text{ day}^{-1}$).

The activity data incorporate temporal variations in farming practice during a year, e.g. number of grazing/housing days per month, percentage slurry and farm yard manure (FYM) spread to grass and/or arable land per month and number of manure storing days per month. In the example for dairy cattle, described above, the annual activity data (number of days per year spent housing) would therefore be replaced by the monthly activity data (number of days per month spent housing), to calculate the monthly UK emission from dairy cows during housing in cubicles.

The temporal activity data in Table 1 are based on survey results and expert opinion. Percentage manures spread each month for all types of livestock were derived from the Surveys of Animal Manure Practices (ADAS) (Smith, Brewer, Dauven, & Wilson, 2000, Smith, Brewer, Crabb, & Dauven, 2001a, Smith, Brewer, Crabb, & Dauven, 2001b). For sheep, manure was assumed to be spread in late summer/autumn. Housing periods for cattle were derived from Smith et al. (2001b) and were allocated to the months when cattle are not grazing. For milking dairy cattle, 3 h per day were allocated to housing throughout the grazing season to account for the cattle coming in for milking. The grazing time was not reduced, however, as (some of the) measurements of emission from grazing accounted for the time when dairy cattle left the field for milking. Studies have also shown that emissions from pasture continue at much the same rate while the cows are being milked. Some responses to these farm practice surveys were by season (i.e. year quarters), explaining why the data are the same within months for each 3-month group.

The following assumptions were made, supported by expert opinion (T. Misselbrook, IGER, and K.A. Smith, B.J. Chambers and J. Webb, ADAS, UK): Cattle grazing was assumed to occur for the complete months of May to September and for part of April and October. Dirty water applications were assumed to occur evenly throughout the year (which is anyway only a minor source). Slurry storage tanks were assumed never to be completely emptied and therefore always have an emitting surface. FYM storage for cattle was assumed to begin in mid-January (when the first clearing of winter-accumulated manure is likely to occur). Most is spread to land in autumn, but some is spread in each month of the year. The probable proportion of manure being stored in any one month was taken into account by reducing the storage period for that month. FYM

storage for pigs and manure storage for poultry was apportioned to fit in with the pattern of manure spreading. Manure storage for sheep was assumed to be from May until July, although it was assumed that not all sheep manure would be stored in any one month.

For lowland sheep, housing was assumed to take place between February and April, with the number of housing days for any one month being adjusted to reflect the proportion of sheep housed for that month. Lowland lambs were assumed to be grazing from mid-January to August, upland lambs were assumed to graze between March and August; the proportion of lambs grazing in any one month being taken into account by adjusting the grazing days for that month.

The temporal pattern of fertiliser use was derived from the British Survey of Fertiliser Practice (BSFP, 2001). Fertiliser emission factors account for emission directly following application (i.e. within 2 weeks) reflecting the experimental data from which they were derived. There is no account taken within the inventory of subsequent emissions over a longer period from crops (e.g. due to senescence).

The central challenge for the model is how to incorporate temporal change effects into the spatial data. Changes in NH_3 emissions with time vary both regarding their spatial location and their magnitude. For instance, cattle may graze some distance from the farm shed in summer, but be in or near the animal houses for the rest of the year. In order to incorporate these changes in the AENEID model, it was necessary to consider three levels of temporal change:

1. *Changes with time in the spatial data* (landcover and parish boundaries)
2. *Changes with time in the attribute data* (Agricultural Census Data and emission potentials)
3. *Changes with time in the modelling parameters* (apportioning percentages, i.e. the rules on how to apportion emission sources onto different types of landcover).

2.1 Calculation of Monthly Ammonia Emission Maps

2.1.1 Agricultural Sources

The availability of monthly agricultural activity data justified the implementation of the ‘snap-shot approach’ (Langran, 1992) at a monthly time-step to calculate seasonal variations in NH_3 emissions. The

methodology used in the monthly version of AENEID is the same as in the original AENEID model (Dragosits et al., 1998), the only difference being the temporal element, applying apportioning percentages and emission potentials representative for each month rather than the whole year. The monthly apportioning percentages were applied to re-distribute the livestock categories onto different landcover types within the parish according to seasonal activities. Livestock emission maps were then calculated by applying monthly emission potentials to the monthly distribution maps.

Changes in emission potentials from month to month have a significant impact on emissions due to seasonal changes in agricultural activities during the year. Temporal activity data, shown in Table 1, were incorporated into the agricultural Inventory of Ammonia Emissions in the UK (Misselbrook et al., 2000, 2003), to calculate the monthly emission potential per animal.

The rules on how to apportion the agricultural statistics to the different landcover categories (‘apportioning percentages’) depend on the emission source strength for each animal husbandry stage (housing, manure storage, spreading of manure, grazing livestock). As the proportion of emissions from each of these stages changes during the year, so do the apportioning percentages, and hence the most likely spatial location of the emission. For instance, the proportion of emissions allocated to those landcover types where grazing occurs (i.e. different quality types of grassland) is higher during the grazing season (summer), than when cattle are housed. Monthly apportioning percentages were therefore calculated based on the emission for each animal husbandry stage, derived from the monthly emission calculations of IAEUK.

Variations in livestock numbers on a monthly basis were not taken into account, as the Agricultural Census Data are only available as annual averages (as snapshots in June). Livestock numbers are, however, likely to be fairly even for most categories throughout the year, with the exception of livestock with seasonal demand such as lambs, turkey and geese. Landcover data and parish data are used to re-distribute the parish aggregated Agricultural Census data in the landscape as NH_3 sources, using the same parish data set and landcover data set for all months of the year.

The monthly breakdown of NH_3 emissions from fertilizers are based on statistics of fertilizer applica-

Table 1 Temporal activity data applied in the study

Cattle		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Grazing (days)													
	Dairy				17	31	30	31	31	30	20		
	Beef				12	31	30	31	31	30	18		
	Calves				25	31	30	31	31	30	22		
Landspreading (%)													
Dairy	Slurry to grass	6	10	10	10	5	5	5	12	12	12	6	6
	FYM to grass	12	9	9	9	3	3	3	9	9	9	12	12
	Slurry to arable	3	10	10	10	1	1	1	20	20	20	3	3
	FYM to arable	5	12	12	12	1	1	1	16	16	16	5	5
Beef	Slurry to grass	10	18	18	18	3	3	3	2	2	2	10	10
	FYM to grass	8	9	9	9	3	3	3	13	13	13	8	8
	Slurry to arable	8	10	10	10	2	2	2	14	14	14	8	8
	FYM to arable	2	3	3	3	4	4	4	24	24	24	2	2
Housing (days)													
	Dairy – milking	31	28	31	15	4	4	4	4	4	14	30	31
	Dairy – non-milking	31	28	31	13	0	0	0	0	0	11	30	31
	Beef	31	28	31	18	0	0	0	0	0	13	30	31
	Calves	31	28	31	5	0	0	0	0	0	9	30	31
Storage (days)													
	Slurry	31	28	31	30	31	30	31	31	30	31	30	31
	FYM	10	28	31	30	31	30	22					
Pigs		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Outdoors (days)													
	Outdoor pigs	31	28	31	30	31	30	31	31	30	31	30	31
Landspreading (%)													
	Slurry to grass	7	10	10	10	9	9	9	7	7	7	7	7
	FYM to grass	10	11	11	11	5	5	5	8	8	8	10	10
	Slurry to arable	7	9	9	9	4	4	4	14	14	14	7	7
	FYM to arable	6	6	6	6	2	2	2	19	19	19	6	6
Housing (days)													
	All pigs	31	28	31	30	31	30	31	31	30	31	30	31
Storage (days)													
	Slurry	31	28	31	30	31	30	31	31	30	31	30	31
	FYM	10	15	15	15	15	15	15	15	15	15	15	15
Poultry		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Outdoors (days)													
	Outdoor hens	31	28	31	30	31	30	31	31	30	31	30	31
Landspreading (%)													
	FYM to grass	3	14	14	14	6	6	6	11	11	11	3	3
	FYM to arable	2	4	4	4	1	1	1	26	26	26	2	2
Housing (days)													
	All poultry	31	28	31	30	31	30	31	31	30	31	30	31
Storage (days)													
	Manure	10	10	10	10	10	10	10	10	10	10	10	10
Sheep		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Grazing (days)													
	Upland sheep	31	28	31	30	31	30	31	31	30	31	30	31
	Upland lambs			31	30	31	30	31	30				
	Lowland sheep	31	18	21	20	31	30	31	31	30	31	30	31

Table 1 (Continued)

Sheep		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Landspreading (%)	Lowland lambs	10	15	25	30	31	30	24	18				
	FYM							25	25	25	25		
Housing (days)	Sheep		10	10	10								
Storage (days)	Sheep												
	FYM					30	30	30					

tion per month (BSFP, 2001), and calculated in relation to the total amount of fertilizer type applied. The monthly fertilizer emission was expressed as a percentage of the annual emission, and these monthly emission proportions were then spatially distributed onto the landcover classes arable and improved grassland, respectively. The fertilizer emission map was added to the livestock emission map to calculate the agricultural NH_3 map for each month.

2.1.2 Non-agricultural Sources

The seasonal pattern for most non-agricultural sources is, in contrast to most agricultural sources, expected to be relatively even throughout the year (humans, pets, wild animals, sewage works, transport, landfill sites, waste incineration, household products etc.). Exceptions to this are emissions from seabird colonies and non-agricultural fertilizers. The non-agricultural sources are, however, much smaller ($44.7 \text{ kt NH}_3\text{-N yr}^{-1}$) (Dragosits, Hellsten, & Sutton, 2004) than the agricultural sources ($206.9 \text{ kt NH}_3\text{-N yr}^{-1}$) (Misselbrook et al., 2003), and therefore considered not to contribute to major seasonal variations in emissions in most of the UK. Non-agricultural sources were therefore spatially dis-aggregated evenly over the year.

3 Results and Discussion

3.1 Monthly Emission Results

The ammonia emissions for the different months (year 2000) are shown in Table 2 and Figs. 1 and 2. An emission peak in March is clearly shown in Fig. 1, mainly as a result of mineral fertilization application in spring and livestock being housed. Emissions then decrease from April to May due to the start of the grazing season and a decrease in fertilizer application. The emissions are estimated to be small during the summer when the livestock are grazing outdoors (particularly due to cattle grazing, as sheep tend to be outside all year round, while pigs and poultry are predominantly housed all year round). The estimated emissions increase again in August towards a small peak in October, as a result of spreading of manure and livestock going back indoors. Emissions then decrease again due to less manure being applied to the fields in wintertime. Cattle are a major source of ammonia emissions (>50% of the agricultural NH_3 emission), and the housing/grazing pattern for cattle therefore significantly influences the overall emission pattern.

Maps of ammonia emissions for the spring (March), versus summer (July) for the year 2000 are shown in

Table 2 Total agricultural ammonia emission values for the UK, year 2000, calculated from the monthly AENEID model

$\text{NH}_3\text{-N (t)}$	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
Total emission	16,115	20,181	28,948	26,199	13,291	12,220	11,912	19,339	18,463	20,338	15,695	16,050	218,751
Fertilizers	10	1,692	8,932	8,748	2,520	1,679	914	497	240	69	14	5	25,319
Livestock	16,105	18,489	20,016	17,451	10,771	10,541	10,998	18,842	18,223	20,269	15,681	16,045	193,432
Cattle	10,816	11,776	12,481	10,127	5,006	4,918	4,954	9,876	9,793	11,641	10,529	10,758	112,674
Sheep	1,184	1,404	1,931	1,818	1,427	1,384	1,706	1,836	1,398	1,497	1,146	1,182	17,913
Pigs	1,962	1,855	2,003	1,954	1,998	1,949	1,998	2,327	2,278	2,327	1,913	1,962	24,525
Poultry	2,143	3,454	3,601	3,552	2,340	2,291	2,340	4,803	4,754	4,803	2,094	2,143	38,321

Fig. 1 Modelled monthly $\text{NH}_3\text{-N}$ emissions (kt) in the UK, year 2000

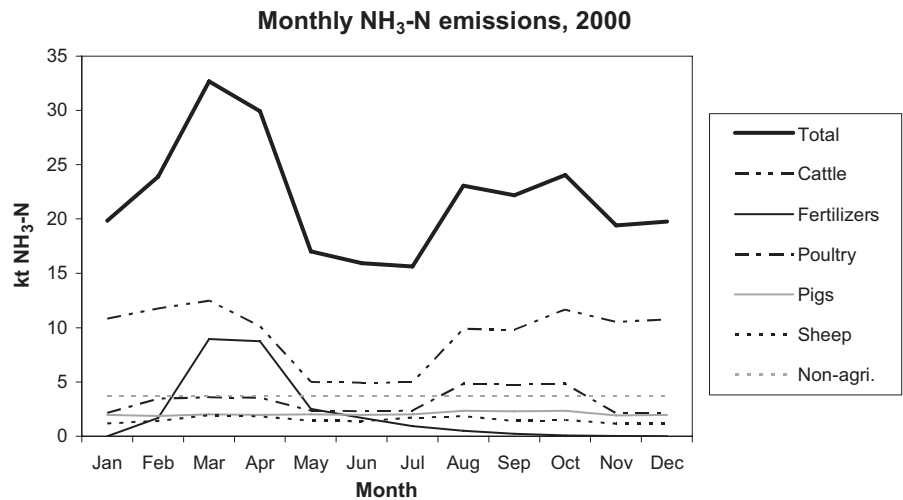


Fig. 3. The emissions are seen to be larger in spring, particularly in the pig, poultry and cattle distributed areas. When modelling temporal NH_3 emissions, it is important to differentiate between temporal differences that are spatial (i.e. the location of emissions varying

with time) compared with differences in the magnitude of emissions (variations in emission source strength with time). For instance, cattle emissions are more localised in winter time, because the emissions are restricted to those landcover types where the cattle

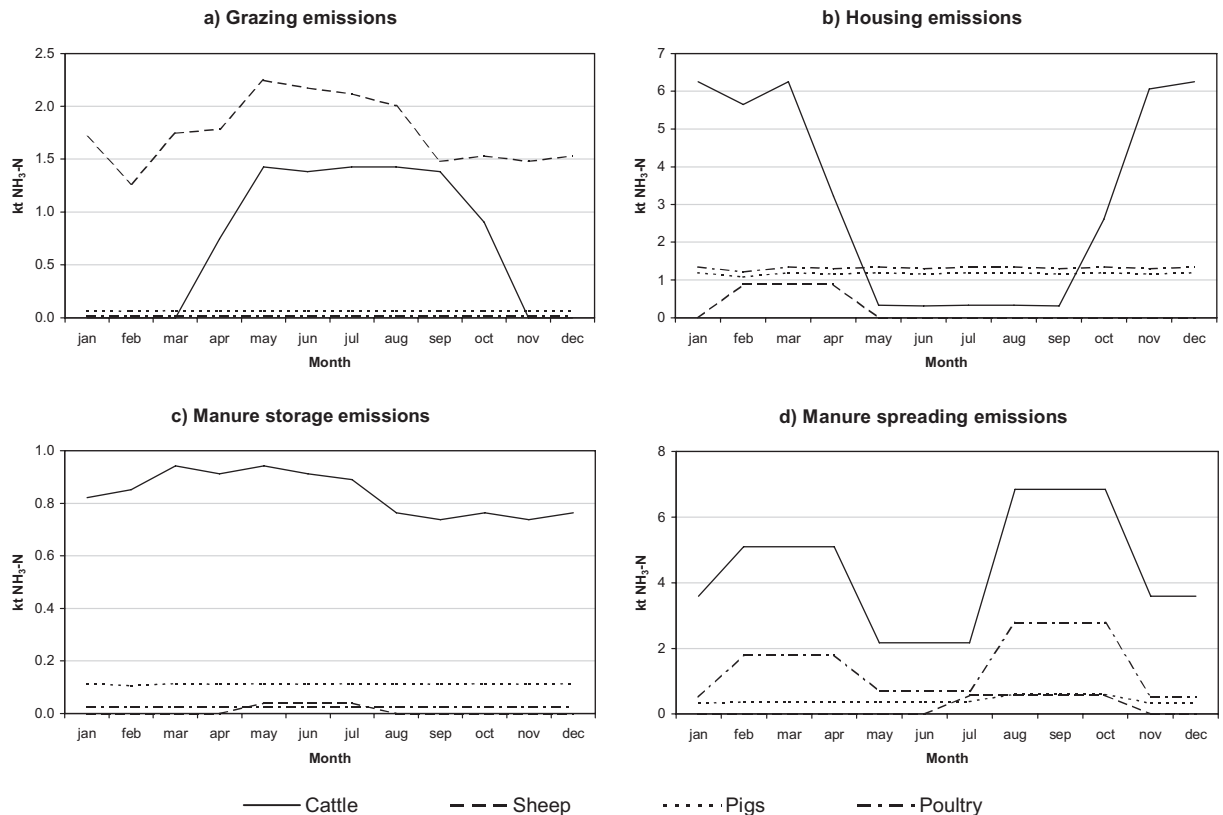


Fig. 2 Modelled monthly temporal emission pattern of $\text{NH}_3\text{-N}$ in the UK for different livestock source activities, **a** grazing, **b** housing, **c** manure storage and **d** manure spreading

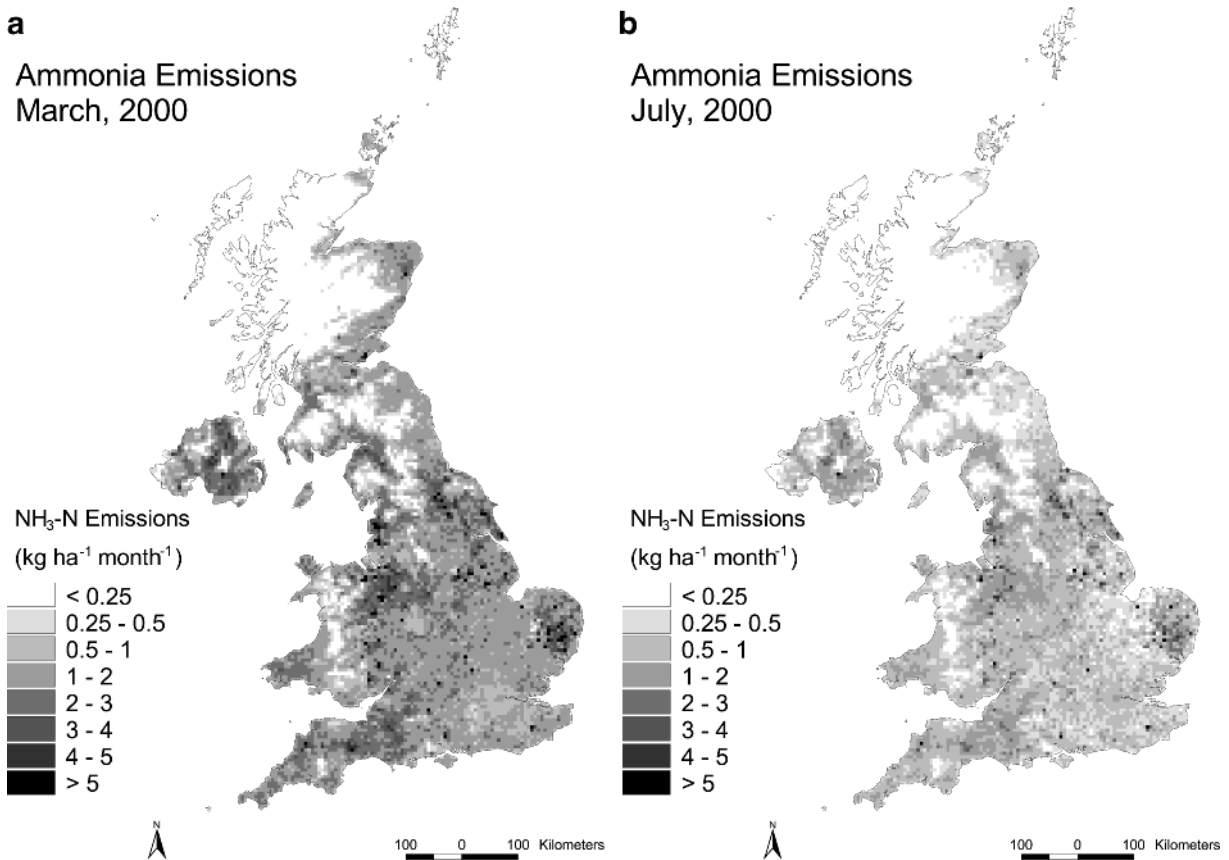


Fig. 3 Modelled ammonia emission maps for spring (March) and summer (July) year 2000

houses are assumed to be located (improved pasture). Cattle emissions are also greater in winter time, because the emission potential from cattle is greater when cattle are housed than when they are out on the fields grazing.

Spatial differences between winter and summer emissions were assessed in two ways. Firstly, Fig. 4a shows the absolute difference in cattle emissions between January and July for 2000. Secondly, Fig. 4b shows the percentage difference between January and July, with the normalization to account for the overall difference in UK cattle emissions between January and July. Thus, Fig. 4a shows the spatial difference in overall magnitude of change, while Fig. 4b shows only the difference in spatial allocation of the emissions. While cattle emissions are modelled to be larger in January than July, (Fig. 4a), Fig. 4b shows that a higher proportion of the emissions occur from hill areas in summer, and consequently, emissions in neighbouring valleys are reduced. This is expected, as the model allocates summer grazing emissions to landcover types common in hill areas, in addition to

housing, storage and manure spreading emissions allocated to good quality grassland. Furthermore, Fig. 4b also shows that dairy areas (e.g. Cheshire) have increased summer emissions to a greater degree than beef areas (e.g. Aberdeenshire), as some housing is still associated with dairy cows even during the summer, i.e. the emission potential for dairy cows is greater than for beef cattle in summer.

3.2 Evaluation of the Monthly AENEID Model

The monthly emission results were compared with measured NH_3 concentration data to assess the robustness of the monthly emission estimates. Monthly measured concentration data were provided from the UK National Ammonia Monitoring Network (NAMN) (Sutton et al., 2001; Tang & Sutton, 2004). One of the purposes of the NAMN is to assess temporal trends of concentrations, both intra-annual trends and inter-annual trends.

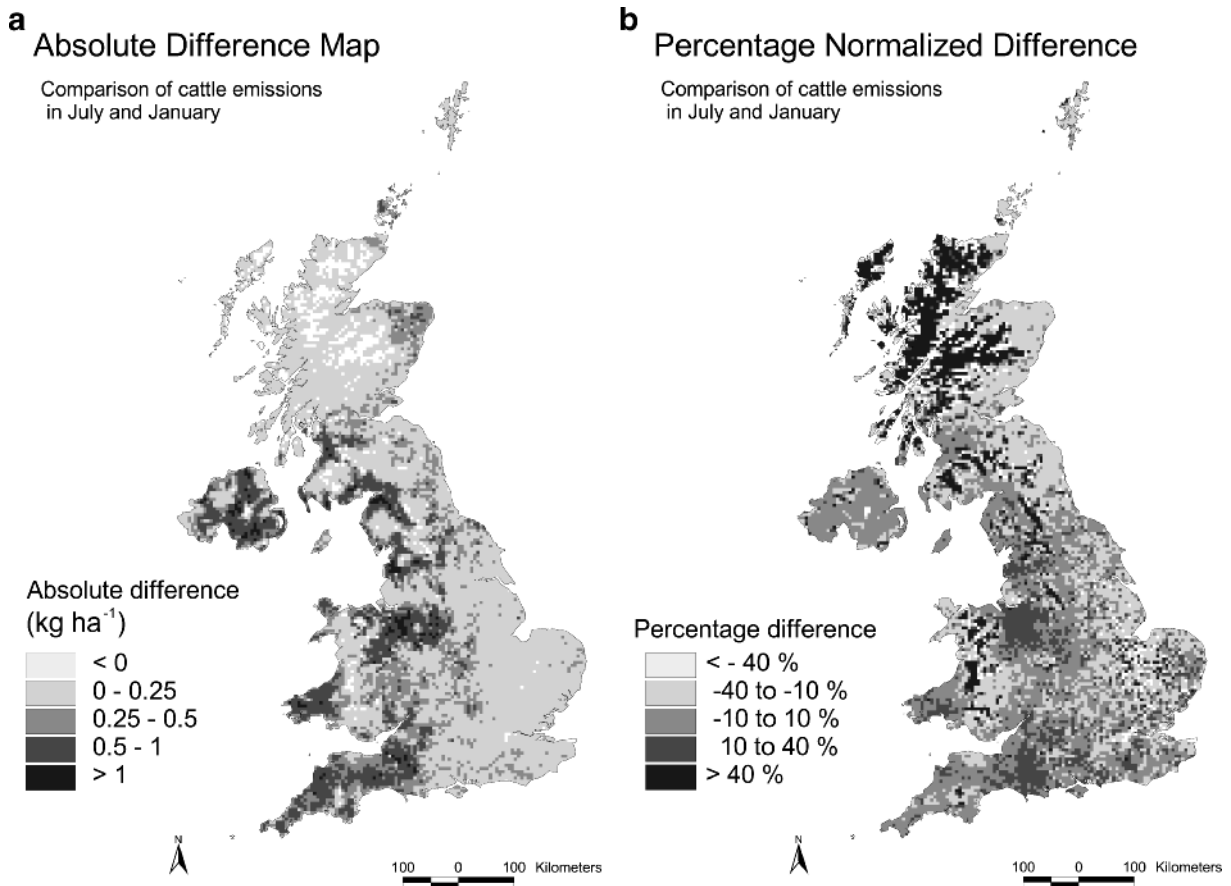


Fig. 4 **a** Absolute difference (kg ha^{-1}) in cattle emissions in summer compared with winter, i.e. January emissions minus July emissions. **b** Percentage of normalized difference in cattle

emissions in summer compared with winter, i.e. normalized July emissions minus January emissions divided by January emissions

The magnitude of ammonia concentration is primarily driven by NH_3 emissions. Such other factors affecting NH_3 concentrations include SO_2 and NO_x emissions affecting rates of ammonium aerosol formation, variations in local windspeed and direction, plus differences in source height and local landscape configuration. However, these factors have an overall small effect compared with the spatial variability in emissions. This is demonstrated by the fact that, for the locations of the UK ammonia monitoring network (Sutton et al., 2001), the correlation between the NH_3 emissions and NH_3 concentration modelled with an atmospheric transport model (both at 5 km grid resolution) is 0.85 (Vieno, 2006). As a result, it is highly informative to compare the modelled emission trend with the measured concentrations.

Measured NH_3 concentrations were available for 83 sites across the UK (Fig. 5), which were assigned

into four different groups (Sutton et al. 2001; Tang & Sutton, 2004) depending on the dominant NH_3 source in the area (cattle, pigs & poultry, sheep or background emissions). The background category represents areas with a low ammonia emission ($<1 \text{ kg NH}_3\text{-N ha}^{-1}$).

The average monthly $\text{NH}_3\text{-N}$ concentrations ($\mu\text{g N m}^{-3}$) for the selected sites for the different dominant source types are shown in Fig. 6, together with the seasonal trend in modelled $\text{NH}_3\text{-N}$ emissions for the corresponding 5-km grid squares derived from the monthly emission maps calculated in this study. From Fig. 6, it is clear that the modelled temporal emission trend is similar to the trend in NH_3 concentrations for pig and poultry dominated areas, with high values in spring and autumn, and smaller values in summer and winter. For cattle dominated areas, the modelled emission trend showed low values in summer, but this was not as evident in the

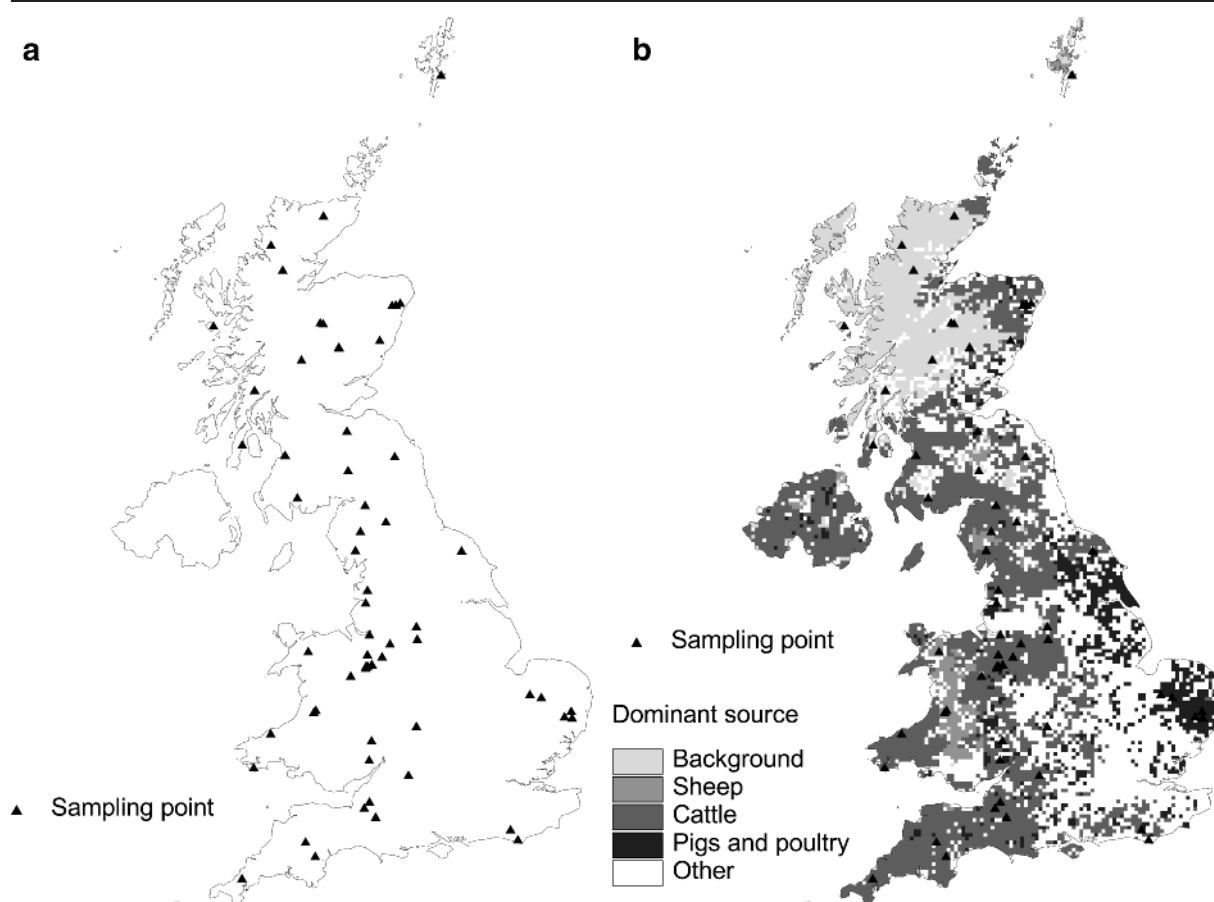
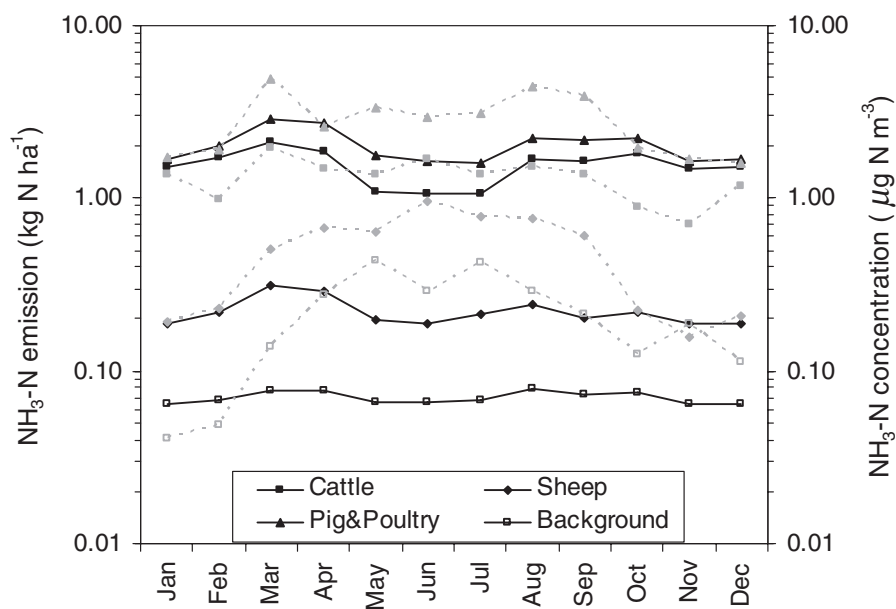


Fig. 5 Map of the 83 sites in the UK National Ammonia Monitoring Network (NAMN) included in the evaluation of the temporal emission result. Dominant sources are based on the modelled AENEID NH_3 emission map 2000. The 'background'

category represents areas with a low ammonia emission ($<1 \text{ kg NH}_3\text{-N ha}^{-1}$). The 'Other' category represents areas dominated either by many different livestock sources, or by fertilizer emissions or non-agricultural sources

Fig. 6 Average modelled $\text{NH}_3\text{-N}$ emissions (kg N ha^{-1}) (—) and measured $\text{NH}_3\text{-N}$ concentration ($\mu\text{g N m}^{-3}$) (---) for the year 2000 at 83 sites across the UK in areas dominated by either cattle, pig & poultry, sheep or background emissions (logarithmic scale). $\text{NH}_3\text{-N}$ concentration values derived from the UK National Ammonia Monitoring Network (Sutton et al., 2001)



ammonia concentration values. This is expected to be due to environmental factors, such as temperature, which have not been accounted for in the current monthly emission estimate, but only the effect of seasonal variations in farming practice on emissions. Thus, warm weather is associated with greater ammonia volatilisation (Monteny & Erisman, 1998). This temperature effect is also a likely explanation for the increased concentrations in sheep dominated areas and background emission areas during the summer, while the modelled emissions for these areas are more constant throughout the year.

The seasonal AENEID model presented in this study was used to derive spatio-temporal patterns in NH_3 emissions in the UK following the 2001 outbreak of Foot and Mouth Disease, where seasonal NH_3 concentrations were derived from monthly AENEID output and compared with measurements (Sutton et al., 2006). The comparison suggests that modelled monthly NH_3 concentrations are larger than the measured concentrations and that the spring and autumn peaks were reproduced by the model, but not the winter peaks in NH_3 concentrations in the measurements. This result does not necessarily imply an overestimation of modelled NH_3 emissions, but could be due to the specific location of sampling points in the modelled grid-squares and uncertainties in the dispersion model. Furthermore, the failure to pick up the winter peak implies that the seasonal emission model fails to incorporate manure spreading to frozen soils which occurs regularly in northern Britain.

3.3 Further Work

The monthly activity data representing seasonal variations in farming practice are highly generalised and are associated with significant regional uncertainties. Furthermore, as described above, the model does not take environmental factors of emissions such as temperature into account. These temporal uncertainties occur in addition to spatial uncertainties and are linked to the location, rate, magnitude and timing of change. Future work should concentrate on improving the temporal activity data and to incorporate environmental factors to reduce some of these uncertainties.

The monthly AENEID model applies the same overall emission per animal evenly across the whole of the UK. In fact the overall emission source strength

is expected to vary across the UK both due to environmental factors (temperature, rainfall, soils etc.) and agricultural practice. A particularly important factor is the length of the cattle grazing season, which is generally longer in the south of the UK. The housing season of cattle has been identified as the most sensitive input parameter to an ammonia emission inventory (Webb et al., 2005). In the current approach, the cattle grazing season and hence the cattle emission potential is assumed constant across the UK. One way to reduce some of this uncertainty in the emission result could be to model the length of the grazing season for each 5×5 km grid cell in the UK and adapt the monthly emission values accordingly.

4 Conclusions

The temporal NH_3 emission approach developed in this study provides a general seasonal picture of ammonia emissions during the year. This information can potentially be applied to identify when monthly threshold levels of ammonia are exceeded and when abatement measures should be implemented. Furthermore, the seasonal NH_3 emission maps can be used as input to atmospheric transport models, which help to interpret the seasonal dynamics in ammonia dispersion and deposition.

The calculated monthly ammonia emission maps showed a strong seasonal emission pattern, with the highest emissions during springtime and the lowest emissions during summer. This emission pattern reflects the temporal activity data, with cattle outdoors grazing during the summer, while most manure and fertilizer application occurs in springtime, with a smaller peak in autumn.

The modelled seasonal emission trend corresponded fairly well with measured NH_3 concentrations. The model should, however, be validated with measurements in greater detail by calculating monthly NH_3 concentration from the emission maps through application of atmospheric transport models.

Future studies should concentrate on reducing uncertainties in the temporal activity data, and to develop approaches to include environmental factors such as temperature. Furthermore, regional differences in the cattle grazing season in the UK should be incorporated, as the cattle grazing season has been identified as a significant temporal uncertainty.

Acknowledgements This work was funded by Defra, through the NARSES project (Project No AM0101), and through the National Atmospheric Emission Inventory (NAEI) (No CO2442) and with underpinning science funding from the NERC Centre for Ecology and Hydrology (CEH).

References

- BSFP (2001). *The British survey of fertiliser practice – Fertiliser use on farm crops from crop year 2000*, British Library Cataloguing in Publication Data.
- Dragosits, U., Hellsten, S., & Sutton, M. A. (2004). 2002 Maps of ammonia emissions from agriculture, waste, nature and other miscellaneous sources for the NAEI. *Report for Defra, AEA Technology and NERC, project number CO2442*, CEH, Edinburgh.
- Dragosits, U., Sutton, M. A., Place, C. J., & Bayley, A. A. (1998). Modelling the spatial distribution of agricultural ammonia emissions in the UK. *Environmental Pollution*, 102, 195–203.
- Fuller, R. M., Smith, G. M., Sanderson, J. M., Hill, R. A., & Thomson, A. G. (2002). The UK Land Cover Map 2000: Construction of a parcel-based vector map from Satellite Images. *Cartographic Journal*, 39, 15–25.
- Horvath, L., & Sutton, M. A. (1998). Long-term record of ammonia and ammonium concentrations at K-puszt, Hungary. *Atmospheric Environment*, 32, 339–344.
- Huber, C., & Kreutzer, K. (2002). Three years of continuous measurements of atmospheric ammonia concentrations over a forest stand at the Högwald site in southern Bavaria. *Plant and Soil*, 240, 13–22.
- Langran, G. (1992). *Time in geographic information systems*. London: Taylor & Francis.
- Misselbrook, T. H., Chadwick, D. R., Chambers, B. J., Smith, K. A., Webb, J., Demmers, T., et al. (2003). Inventory of ammonia emissions from UK agriculture – 2002. *Inventory submission report, December 2003, Defra contract AM0127*.
- Misselbrook, T. H., Van der Weerden, T. J., Pain, B. F., Jarvis, S. C., Chambers, B. J., Smith, K. A., et al. (2000). Ammonia emissions factors for UK agriculture. *Atmospheric Environment*, 34, 871–880.
- Monteny, G. J., & Erisman, J. W. (1998). Ammonia emission from dairy cow buildings: A review of measurement techniques, influencing factors and possibilities for reduction. *Netherlands Journal of Agricultural Science*, 46, 225–247.
- Smith, K. A., Brewer, A. J., Crabb, J., & Dauven, A. (2001a) A survey of the production and use of animal manures in England and Wales. II. Poultry manure. *Soil Use and Management*, 17, 48–56.
- Smith, K. A., Brewer, A. J., Crabb, J., & Dauven, A. (2001b) A survey of the production and use of animal manures in England and Wales. III. Cattle manures. *Soil Use and Management*, 17, 77–87.
- Smith, K. A., Brewer, A. J., Dauven, A., & Wilson, D. W. (2000). A survey of the production and use of animal manures in England and Wales. I. Pig manure. *Soil Use and Management*, 16, 124–132.
- Sutton, M. A., Dragosits, U., Simmons, I., Tang, Y. S., Hellsten, S., Love, L., et al. (2006). Monitoring & modelling trace-gas changes following the 2001 outbreak of Foot & Mouth Disease to reduce the uncertainties in agricultural emissions abatement. *Environmental Science & Policy*, 9, 407–422.
- Sutton, M. A., Tang, Y. S., Dragosits, U., Fournier, N., Dore, T., Smith, R. I., et al. (2001). A spatial analysis of atmospheric ammonia and ammonium in the UK. *The Scientific World*, 1, 275–286.
- Tang, Y. S., & Sutton, M. A. (2004). Quality management in the UK National Ammonia Monitoring Network. In A. Borowiak, T. Hafkenscheid, K. Saunders, & P. Woods (Eds.), *Proceedings of the International Conference “QA/QC in the field of emission and Air Quality Measurements”*, Prague (CZ), European Commission DG Joint Research Centre, EUR 20973 (ISBN 92-894-6523-9), pp. 297–307.
- Vieno, M. (2006). The use of an Atmospheric Chemistry-Transport Model (FRAME) over the UK and the development of its numerical and physical schemes. PhD Thesis, University of Edinburgh, Edinburgh.
- Webb, J., Anthony, S. G., Brown, L., Lyons-Visser, H., Ross, C., Cottrill, B., et al. (2005). The impact of increasing the length of the cattle grazing season on emissions of ammonia and nitrous oxide and on nitrate leaching in England and Wales. *Agricultural Ecosystems & Environment*, 105, 307–321.
- Yamamoto, N., Nishiura, H., Honjo, T., Ishikawa, Y., & Suzuki, K. (1995). A long-term study of atmospheric ammonia and particulate ammonium concentrations in Yokohama, Japan. *Atmospheric Environment*, 29, 97–103.

Inter-annual Variations of Ozone and Nitrogen Dioxide Over Europe During 1958–2003 Simulated with a Regional CTM

Camilla Andersson · Joakim Langner

Received: 17 June 2005 / Revised: 21 December 2005 / Accepted: 22 January 2006 / Published online: 11 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Inter-annual variability of surface ozone (O_3) and nitrogen dioxide (NO_2) over Europe has been studied over the period 1958–2003 using a three-dimensional Chemistry-Transport Model coupled to meteorological data from the ERA40 data set produced at the European Centre of Medium-range Weather Forecasts (ECMWF). Emissions and boundary conditions were kept at present levels throughout the simulation period. It was found that the annual mean NO_2 concentration varies between $\pm 50\%$ and the summer mean O_3 concentration varies between -10 and $+20$ percent (%) compared to the 46-year average over the model domain. There is also variation in ozone and NO_2 over longer time scales. The last 22 years display high concentrations of ozone in central and south-western Europe and low concentrations in north-eastern Europe. The first 22 years display very high concentrations of NO_2 over the North Sea. There is indication of trends in ozone and nitrogen dioxide but this has to be investigated further. Such information is one factor

that should be taken into account when considering future control strategies.

Keywords air pollution · MATCH · meteorological variability · policy · simulation

1 Introduction

Surface ozone (O_3) has negative effects on human health as well as on the growth of forests and crops and is one of the major pollutants in Europe today. The emission of oxides of nitrogen (NO_x) has decreased in Europe over the last 15 years, which has led to decrease in high O_3 levels at rural sites. At the same time minimum and mean O_3 levels have increased, probably due to an increase in background O_3 (Solberg, Derwent, Hov, Langner, & Lindskog, 2005). Another air pollutant, is nitrogen dioxide (NO_2). NO_2 concentrations have been decreasing in many parts of Europe due to NO_x emission reductions.

Recently elevated levels of surface O_3 have been reported for various areas in Europe, especially 2003 was an extreme year in central and western Europe, with excess deaths reported (Solberg et al., 2005). Unusually dry and warm weather, up to three degrees higher than the last 30-year mean, was one reason for the high O_3 levels. Apart from increasing background levels, a possible climate change could affect the

C. Andersson (✉)
Department of Applied Environmental Research,
Stockholm University,
Frescativägen 54 a, 10691 Stockholm, Sweden
e-mail: camilla.andersson@smhi.se

C. Andersson · J. Langner
Swedish Meteorological and Hydrological Institute,
60176 Norrköping, Sweden

levels of air pollution in the region (Langner, Bergström, & Foltescu, 2005).

New European policies on air pollution are under development e.g. in the Clean Air For Europe (CAFE) programme of the European Commission. To aid this work it is important to assess the variability in concentrations of O₃ and NO₂ due to inter-annual variations in weather. This is also important in view of possible future climate change, in which case the years now considered extreme could occur more frequently (Grennfelt & Hov, 2005).

The main objective of this study was to isolate the variations in air pollution due to meteorological variability with the aid of model simulations for 1958–2003. Emissions and boundary conditions were kept at present levels throughout the whole simulation; to allow for a proper evaluation of model performance for present conditions and to isolate dependence on meteorological variation. The present paper presents selected results showing the variability in summer mean O₃ and annual mean NO₂ over Europe for the period 1958 to 2003.

This is an exploratory study using the wealth of information available in the recent ERA40 re-analysis to pin-point the importance of meteorological variability on inter-annual variations in air pollution.

2 Materials and Methods

2.1 Chemical Transport Model

The three dimensional, Eulerian, Multi-scale Atmospheric Transport and Chemistry (MATCH) model, developed at the Swedish Meteorological and Hydrological Institute, was used in this study. The MATCH model can be used to simulate emission, transport, wet and dry deposition and chemical conversion on various scales, from urban (Gidhagen, Johansson, Langner, & Foltescu, 2005) to regional (e.g. Langner et al., 2005). The advection scheme used in the model is Bott-type (Bott, 1989). The dry deposition is modelled using a resistance approach. The wet deposition is assumed to be proportional to the precipitation intensity. A complete description of the transport model can be found in Robertson, Langner, and Engardt (1999). A description of the gas-phase chemistry can be found in Langner, Bergström, and Pleijel (1998). It is based on the EMEP MSC-W model (Simpson, Andersson-

Sköld, & Jenkin, 1993), with some modifications. The photochemical model includes about 130 reactions and 67 chemical components.

2.2 Emission Data and Boundary Conditions

Anthropogenic emissions of NO_x, oxidised sulphur compounds (SO_x), carbon monoxide (CO), non-methane volatile organic compounds (NMVOC) and ammonia (NH₃) were derived from the emission database provided by EMEP MSC/W. The EMEP expert emissions (Vestreng, Adams, & Goodwin, 2004) for year 2000 were used throughout the whole simulation. Emissions of isoprene were calculated in MATCH using the E-94 isoprene emission methodology proposed by Simpson, Guenther, Hewitt, and Steinbrecher (1995). Boundary conditions were based partly on observations at background locations and partly on large-scale simulations. Both boundary conditions and the EMEP expert emissions were introduced in the simulation with temporal variation, from seasonal to diurnal variation; however there was no variation in these from year to year, i.e. there was no trend in emissions and boundary conditions. This means that no extreme emissions occurring for single years, such as volcanic eruptions, were taken into account in this simulation. Further, this also means that observed changes in global budgets of various compounds which may have occurred was not accounted for either. All variation in air pollution is hence due to changes in the meteorology.

2.3 Meteorological Input Data

Inputs to the model are emissions, physiography, deposition velocities, boundary conditions and driving meteorological data. In this study the ERA40 meteorological dataset (Uppala et al., 2004) from the European Centre of Medium-range Weather Forecasts (ECMWF) is used. ERA40 is a re-analysis that attempts to merge all available meteorological observation data into a consistent, global, three dimensional description of the evolution of the state of the atmosphere as a function of time. Although there are several problems in preparing a re-analysis, related to observation coverage and quality as well as biases in the analysis model, ERA40 is currently the best re-analysis available for regional studies over Europe with the best spatial resolution and best availability of output

variables needed in a regional CTM. 6-hourly data of the lowest 21 model levels reaching 5 km were used. All data were taken from analyses except precipitation and albedo, which were taken from forecasts.

The ERA40 data were interpolated from the original 125×125 km horizontal resolution to $0.4^\circ \times 0.4^\circ$ (ca. 44 km) used by MATCH to make use of the 50 km emission resolution. The ERA40 meteorological data set stretches from September 1957 to August 2002. For the purpose of this study it was used to run the model from 1958 to 2001. However, there was a wish to include also the years 2002 and 2003. To do this operational ECMWF model data were used, including an overlap of 2001 to assess the difference in results due to different meteorological data.

3 Comparison with Observed Concentrations and Deposition for 1999

Measured hourly O_3 values and daily values of sulphur dioxide (SO_2), NO_2 , sulphate (SO_4^{2-}), nitrate

(NO_3^-), nitrous acid (HNO_3), ammonium (NH_4^+) and NH_3 , as well as wet deposition of SO_4^{2-} , NO_3^- and NH_4^+ at EMEP stations were retrieved from the EMEP homepage (EMEP/CCC, 1999; Hjellbrekke, 2001) and were used to assess the model performance for year 1999.

In Table 1 the global and spatial mean of modelled and measured concentrations and wet deposition, along with statistics is shown. The model underestimates the O_3 concentration by around 10% on average. The correlation is best for the daily maximum values, i.e. the model is better at predicting the peak of each day than the mean O_3 . The global correlation is higher than the spatial correlation, which shows that the negative bias is not uniform throughout the whole region. The model compares well with other European scale models reported by van Loon et al. (2004), showing correlations ranging from 0.69 to 0.79 and bias for daily maximums ranging from -13 to +11%. For concentrations of other compounds, the bias is below 10%, except for SO_2 and NH_4^+ , which are overestimated by about 30

Table 1 Observed (OBS) and modelled (MATCH) mean (O_3 : ppbv; other conc.: μg (S/N) m^{-3} ; wet dep.: mg (S/N) m^{-2}), bias (%) and correlation for the year 1999 of hourly mean or daily max O_3 , daily concentrations of air pollution or monthly accumulated wet deposition

Global						Spatial				
	OBS Mean	MATCH Mean	Percent bias	corr	Number cases	OBS Mean	MATCH Mean	Percent bias	Corr	Percent cases
O_3 mean(h)	32.29	29.19	-9.6	0.59	842706	32.62	29.30	-10.2	0.46	106
O_3 max(d)	42.70	37.93	-11.2	0.72	36059	43.05	38.10	-11.5	0.63	106
Na^+	0.59	0.65	9.5	0.59	7458	0.70	0.67	-4.4	0.53	8
SO_2	0.94	1.21	28.5	0.35	29537	0.95	1.32	39.5	0.51	88
SO_4^{2-}	0.76	0.70	-8.1	0.294	26365	0.77	0.71	-7.8	0.73	82
NO_2	2.07	1.86	-10.1	0.485	22688	2.11	2.06	-2.4	0.61	68
NO_3^-	0.51	0.48	-5.1	0.503	6725	0.49	0.47	-4.0	0.87	20
HNO_3+NO_3	0.45	0.45	0.3	0.393	13424	0.46	0.46	0.3	0.75	40
NH_4^+	0.87	1.00	14.3	0.443	8149	0.84	0.96	14.4	0.71	25
NH_3+NH_4	1.23	1.12	-9.2	0.55	13656	1.25	1.13	-9.3	0.72	41
SO_4^{2-} -wet	40.54	40.20	-0.8	0.401	905	40.49	39.97	-1.3	0.57	78
NO_3^- -wet	27.44	23.01	-16.2	0.37	905	27.04	23.03	-14.8	0.56	78
NH_4^+ -wet	30.06	25.03	-16.7	0.296	905	29.77	25.07	-15.8	0.47	78

In the evaluation of O_3 two stations were excluded, SI31 and SI33, on recommendation from Kovac (2002)

The global bias is the fractional bias, in percent, of the modelled mean concentration, daily max O_3 and monthly accumulated wet deposition of NH_4^+ , SO_4^{2-} and NO_3^- compared to the measured corresponding values, while the spatial bias is the fractional bias of the spatial mean

Global correlation for O_3 is the mean of the correlation coefficients at each site, weighted with the number of paired values, while it is the correlation coefficient between all values for the other components. The spatial correlation is the correlation between the means at each site

and 14% respectively. It is a known fact that it is hard to model primary emitted compounds, since they have a large vertical gradient in parts of Europe. Both correlations and bias of these compare well with values reported for other models by van Loon et al. (2004). The SO_4^{2-} correlation stand out as low, on the other hand other compounds such as NO_3^- and NH_4^+ show higher correlations than is usually achieved. The bias is low for wet deposition; however the correlations are low also. One reason for this could be that the place and the amount of precipitation as predicted by the ERA40 forecast are not as accurate as the model needs for calculating deposition. Another reason could be that the horizontal resolution of ERA40 is low compared the regional scale meteorological data from HIRLAM that has been used previously. However, all models trying to simulate wet deposition have difficulties (van Loon et al., 2004).

To assess the difference between the simulation for 2001 using operational meteorological data and ERA40, four grid cells in different areas of the model domain were chosen for comparison. Shown in Table 2 are statistics from this comparison. The results from the two model runs for O_3 compare very well: the bias is very close to zero and the correlations are above 0.90. The bias for the NO_2 -comparison is somewhat greater, but still much lower than the inter-annual variation. The correlation for NO_2 is high in general. Further study revealed that the difference in results was greater in mountainous areas, probably due to the change in resolution which could have an impact, especially in areas with spatial complexity.

To summarize the comparisons, it is apparent that the modelled O_3 and NO_2 show good agreement with

measurements for 1999, especially in comparison with other models. The difference between the two model runs for 2001 is very small.

4 Results

4.1 Variability of Ozone

Using annual mean and summer half-year mean (April–September) the 1958–2003 mean and the fractional range (frgm) and standard deviation (fsd) are calculated. The result is presented in Fig. 1. As expected the summer mean gives higher values overall than the yearly mean, lower mean values are found where major NO_x emissions are present, e.g. in central Great Britain and the Netherlands. In northern Italy and along the Mediterranean coastline the greatest fsd is displayed, while the frgm show high values also in central and northern Europe. The range reaches 25 ppbv at the most, along the northern Italian coast.

In Fig. 2 the deviations (%) of summer mean O_3 from the mean over all summer means are shown for each simulated year. The deviation varies from –10 to +20% for individual years and locations. Among the years with higher values than usual are 1959 in western Europe, with a maximum bias of 16.7% and 2003 in most of Europe, with central Europe having extreme values, the maximum bias being 52%. The location where the O_3 concentrations are higher than usual vary, for instance in 1959 higher bias is shown in western Europe, while two years later higher bias occur mostly in central and eastern Europe. There

Table 2 Comparison between modelled hourly means of ozone and daily means of nitrogen dioxide from using operational ECMWF meteorological data and ERA40 data for the year 2001. Mean (ppbv), bias (%) and correlation at four spots: the Atlantic Ocean (47.5° N, –7.5°E), Russia (52.5°N, 35.0°E), France (47.5°N, 2.5°E) and Italy (45.0°N/46.0°N, 10.0°E/12.5°E)

	Ozone					Nitrogen dioxide				
	ERA40 Mean	OPER Mean	Percent bias	Corr	Number cases	ERA40 Mean	OPER Mean	Percent bias	Corr	Number cases
Atlantic	40.32	39.91	–1.04	0.94	8702	1.26	1.32	4.91	0.93	353
Russia	26.22	26.13	–0.32	0.92	8702	0.87	0.84	–2.94	0.97	353
France	28.79	28.84	0.16	0.95	8702	2.55	2.49	–2.26	0.96	353
Italy	31.52	31.59	0.23	0.93	8702	11.87	12.42	4.67	0.85	353

The location of the Italian spot was changed when going from O_3 to NO_2 for better representativity.

seems to be a trend towards higher levels of O_3 in central Europe for the later part of the 1990s. This is shown more clearly in Fig. 3. Displayed are five 22-year summer averages with six-year difference between the starting points along with the deviations of these means from the 1958–2003 summer mean. There is a low frequency variation, the highest concentration occur in central Europe for the period 1982–2003, the deviation being 2–5% in large areas. The lowest concentrations are occurring in central Europe for the period 1970–1991. At least the three right-most figures seem to indicate a trend towards higher summer O_3 concentrations due to changes in meteorology in central, south-western and south-eastern Europe. All figures seem to indicate a negative trend in north-eastern Europe. Omitting the year 2003 in the study will still give a great positive deviation in large parts of central, south-eastern and south-western Europe.

4.2 Variability of Nitrogen Dioxide

In Fig. 4 statistics for the whole period calculated from annual means of NO_2 is shown: 1958–2003 mean concentration, fractional range (frgm) and standard deviation (fsd). We see that in south-eastern Great Britain having major NO_x -emissions, NO_2 levels are highest. NO_2 levels are also high in larger cities, e.g. Moscow and Paris and along the coastline of northern Italy and southern Spain.

Figure 5 shows the bias of the annual mean compared to the mean over the whole period. We see that the deviation is quite large, the maximum deviation ranging between ± 50 , with one exception in 1963, reaching +80%. The largest deviation occurs over the Atlantic Ocean, probably because of the strong horizontal gradient from Great Britain.

There is a low-frequency variation in NO_2 . The bias for the years 1958–1979 shows fairly large

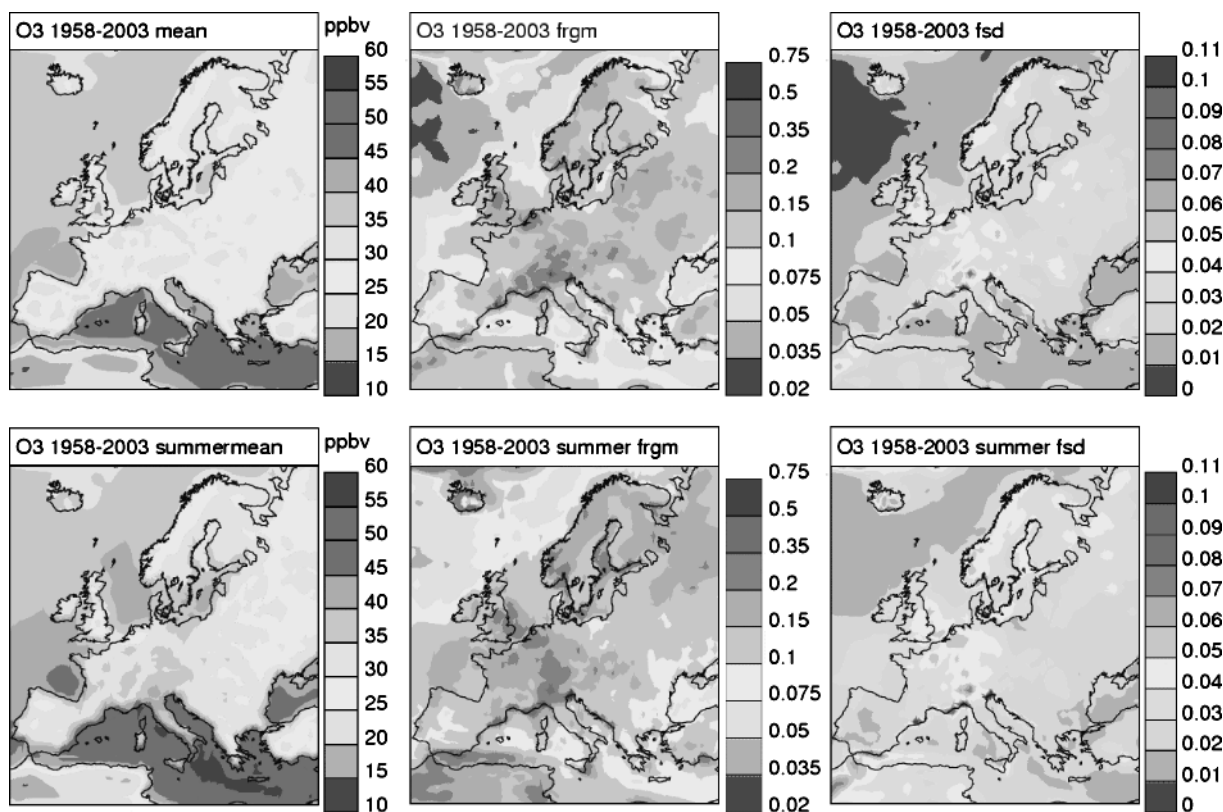


Fig. 1 Mean (ppbv), fractional range and standard deviation of ozone concentration in air, for the time period 1958–2003. The top three figures display summarizing statistics for the whole

year, the lower three figures display summarizing statistics for the summer half year: April–September

positive values over the Atlantic Ocean, excluding the year 1963 will reduce the area having a bias above 5% somewhat. There is possibly a negative trend over the North Sea for the first three pictures. Over land there is no apparent overall trend in NO_2 due to meteorological variations as can be seen in Fig. 6.

5 Conclusions

Inter-annual variability of surface O_3 and NO_2 over Europe due to meteorological variability has been studied over the period 1958–2003. The following conclusions are drawn: The inter-annual variation in summer O_3 levels is usually between $\pm 10\%$ compared to the 1958–2003 summer mean over Europe. However, some years have higher deviations with up

to 20% over large areas. The inter-annual variability in NO_2 is greater than that of O_3 , with maximum deviations reaching $\pm 50\%$ in limited areas. There is a low-frequency variation in both summer O_3 and NO_2 . The years 1982–2003 display higher deviation in summer ozone concentrations in central, south-eastern and south-western Europe than any other period or area. There is a very high deviation in NO_2 over the North Sea for the period 1958–1979. There is possibly a trend towards higher summer O_3 means over south-western, south-eastern and central Europe from the 1970s and a trend towards lower summer O_3 means over north-eastern Europe during the whole period due to meteorological variability only. Further trend-analysis is needed for both NO_2 and O_3 for finding significant trends. Statistics over larger areas is also of interest as well as finding crucial meteorological parameters, and to look at for



Fig. 2 Fractional bias (percent) of summer mean ozone concentrations compared to the 46-year summer mean (1958–2003)

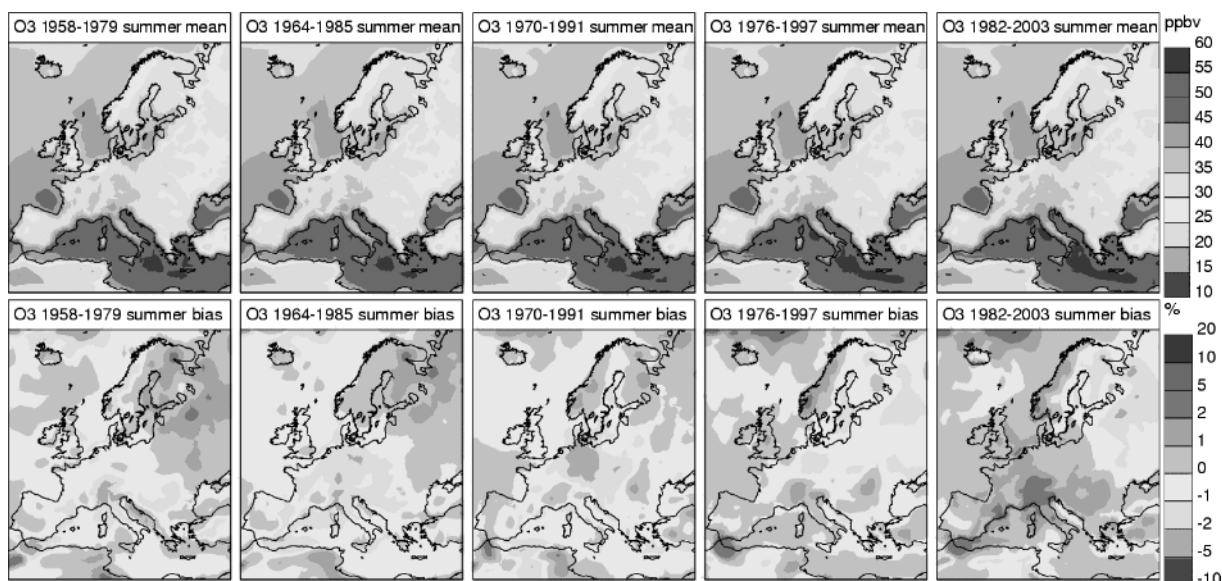


Fig. 3 22-year summer means (ppbv) and fractional bias (percent) of 22-year summer mean ozone concentration compared to the total 46-year summer mean for the time periods: 1958–1979, 1964–1985, 1970–1991, 1976–1997 and 1982–2003

example trends in isoprene. Isoprene would be interesting due to the fact that it is emitted on-line and hence its emission varies. Finally, future work also includes simulations varying boundary conditions to account for large scale changes in tropospheric chemistry and distributions of pollutants and changes in European emissions.

Climate change could mean that meteorological extreme years such as 2003 and 2002 will occur more often (Pal, Giorgi, & Bi, 2004). 2002 was an extreme year in precipitation, causing flooding, while warm and dry weather occurred in central and western Europe in 2003. Central Europe could face more

frequent drought and warmer temperatures, which could lead to increased risk of high O_3 concentrations, while north-eastern Europe could have increase in precipitation and cloudiness. Drought and high temperatures would mean higher O_3 values, while more precipitation and colder would mean less O_3 . This study indicates that part of the increase in surface ozone concentration seen over Europe over the last decade could be due to changes in meteorology. There seems to be an upward trend in O_3 in central, western and southern Europe due to meteorological conditions, by 1–5% the last 12 years, while north-eastern Europe seem to have decreasing levels of O_3 , by 1–

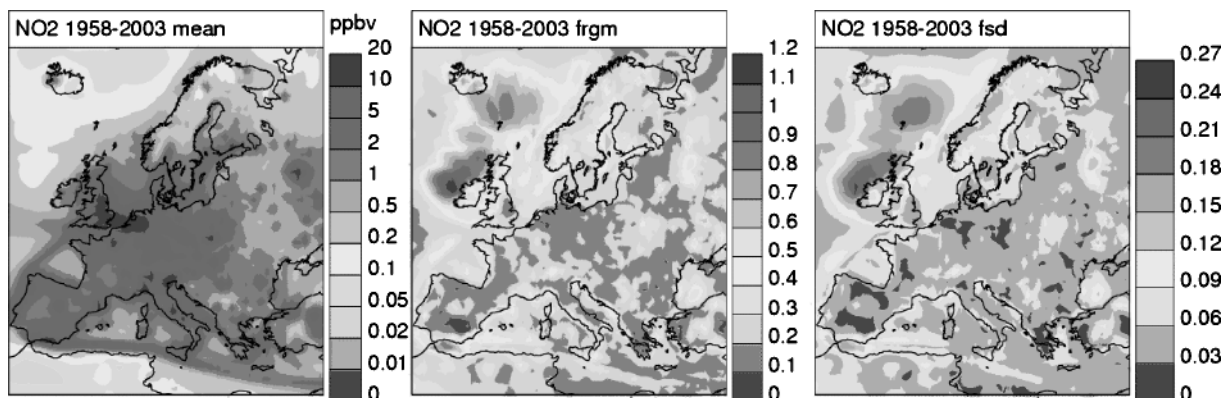


Fig. 4 Mean (ppbv), fractional range and standard deviation of nitrogen dioxide, for the time period 1958–2003



Fig. 5 Fractional bias (percent) of annual mean nitrogen dioxide concentration compared to the 46-year mean (1958–2003)

2% the last 12 years. Increasing levels due to climate change need to be taken into account if air quality standards are to be met in the future. Since 1980 the emissions of NO_x in Europe have been reduced by 30% and NMVOC by 35% (Grennfelt & Hov, 2005).

Correcting for meteorological variability, this has resulted in a decrease in maximum O_3 levels by about $1\text{--}2\%$ year $^{-1}$, however mean levels have not decreased and background levels have in fact increased by $0.3\text{--}0.5$ ppbv year $^{-1}$ (Solberg et al.,

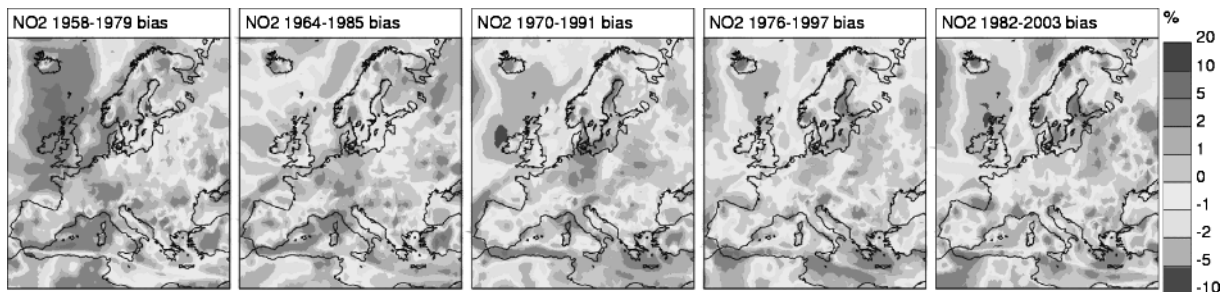


Fig. 6 Fractional bias (percent) of 22-year nitrogen dioxide concentration compared to the total 46-year mean for the time periods: 1958–1979, 1964–1985, 1970–1991, 1976–1997 and 1982–2003

2005). If the frequency of extreme years such as 2003 is increasing with a positive bias of O₃ up to 20% in large areas, the emission levels will have to be reduced further to counterbalance the increase. In addition, international agreements outside Europe are of importance to reduce the background levels.

This work gives an overview over the inter-annual and low-frequency variations in air pollution caused by changes in meteorology over a longer period and an indication of trends. We believe that such information is one factor which should be taken into account considering future control strategies in Europe.

Inter-annual variations and trends in deposition of sulphur and nitrogen, as well as PM₁₀ and PM_{2.5} will be reported elsewhere.

Acknowledgements This work was part of the project Network for the support of European Policies on Air Pollution (NEPAP), which was supported by the European Commission through the contract EUK2-CT-2002-80019. Special thanks to Robert Bergström and Valentin Foltescu at SMHI for their help with the emission set-up and for the processed measurement data.

References

- Bott, A. (1989). A positive definite advection scheme obtained by non-linear renormalization of advective fluxes. *Monthly Weather Review*, 117, 1006–1015.
- EMEP/CCC (1999). EMEP measurement data (available online URL: <http://www.emep.int>, Jan. and Jul. 2001 (ozone) and Apr. 2003 (other compounds)).
- Gidhagen, L., Johansson, C., Langner, J., & Foltescu, V. L. (2005). Urban scale modeling of particle number concentration in Stockholm. *Atmospheric Environment*, 39, 1711–1725.
- Grennfelt, P., & Hov, Ø. (2005). Regional air pollution at a turning point. *Ambio*, XXXIV(1), 47–53.
- Hjellbrekke, A. G. (2001). Data report 1999. Acidifying and eutrophying compounds. Part 2: Monthly and seasonal summaries., EMEP/CCC-report 03/2001 (available online URL: <http://www.nilu.no>, 25 May 2005).
- Kovac, N. (2002). Mandatory data checking for the EMEP assessment, Environmental Agency of Slovenia, Monitoring office, air quality section, 2 pp. (available online URL: <http://www.nilu.no/projects/ccc/sitedescriptions/si/index.html>, 27 May 2005).
- Langner, J., Bergström, R., & Foltescu, V. L. (2005). Impact of climate change on surface ozone and deposition of sulphur and nitrogen in Europe. *Atmospheric Environment*, 39, 1129–1141.
- Langner, J., Bergström, R., & Pleijel, K. (1998). European scale modeling of sulphur, oxidized nitrogen and photochemical oxidants. Model development and evaluation for the 1994 growing season, SMHI report, RMK No. 82, Swedish Met. and Hydrol. Inst., Norrköping, Sweden.
- Pal, J. S., Giorgi, F., & Bi, X. Q. (2004). Consistency of recent European summer precipitation trends and extremes with future regional climate projections. *Geophysical Research Letters*, 31, L13202, doi 10.1029/2004GL019836.
- Robertson, L., Langner, J., & Engardt, M. (1999). An Eulerian limited-area atmospheric transport model. *Journal of Applied Meteorology*, 38, 190–210.
- Simpson, D., Andersson-Sköld, Y., & Jenkin, M. E. (1993). Updating the chemical scheme for the EMEP MSC-W oxidant model: Current status. EMEP MSC-W note 2/93.
- Simpson, D., Guenther, A., Hewitt, C. N., & Steinbrecher, R. (1995). Biogenic emissions in Europe. 1. Estimates and uncertainties. *Journal of Geophysical Research*, 100, 22875.
- Solberg, S., Derwent, R. G., Hov, Ø., Langner, J., & Lindskog, A. (2005). European abatement of surface ozone in a global perspective. *Ambio*, XXXIV(1), 47–53.
- Uppala, S., Kållberg, P., Hernandez, A., Saarinen, S., Fiorino, M., Li, X., et al. (2004). ERA40:ECMWF 45-year reanalysis of the global atmosphere and surface conditions 1957–2002. *ECMWF Newsletter*, 101, 2–21.
- van Loon, M., Roemer, M. G. M., Builtjes, P. J. H., Bessagnet, B., Rouil, L., Christensen, J., et al. (2004). Model inter-comparison. In the framework of the review of the unified EMEP model', TNO-report, TNO-MEP – R 2004/282, 53 pp.
- Vestreng, V., Adams, M., & Goodwin, J. (2004). Inventory review 2004, Emission Data reported to CLRTAP and under the NEC Directive, EMEP/EEA joint review report, EMEP/MSC-W note 1/2004. ISSN 0804-2446.

Field Intercomparison of Main Components in Air in EMEP

Wenche Aas · Jan Schaug · Jan Erik Hanssen

Received: 12 June 2005 / Accepted: 22 January 2006 / Published online: 13 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Within the European monitoring network (EMEP, <http://www.emep.int>) several different sampling procedures for measuring the main air components have been applied. This has contributed to systematic concentration differences and a comparability problem. Since 1997 co-located experiments in 15 countries have been carried out to quantify these differences. In addition, three major measurement campaigns were organized by EMEP between 1985 and 1991. Differences among results depend on the concentration level and methods used. The decrease in SO₂ concentrations over the last twenty years has placed greater demands on the methodology. Absorbing solutions methods for SO₂, (H₂O₂ and tetrachloromercurate (TCM)) typically have higher detection limits than the reference method, which uses KOH impregnated filters. The TCM method also has problems with negative interference, especially in summertime. UV fluorescence monitors have in a few cases proven to give good results, but interferences, detection limit and poor maintenance can be problems. For NO₂, many countries are using the TGS absorption solution method, which has a higher detection limit than the reference method using NaI impregnated glass sinters. The Salzmann method gives unreliable results

at concentrations below 1 µgN/m³, and even at higher concentrations the uncertainty is rather unsatisfactory. The chemiluminescence monitor with molybdenum converters tends to systematically overestimate NO₂ concentrations, possibly because zero-drift problems and the non-specific response to NO₂. Particulate sulphate measurements in general have lower bias and uncertainties than gas and other aerosol measurements.

Keywords EMEP · quality control · reference method · method comparison · sulphur dioxide · nitrogen dioxide · sulphate · nitrate

1 Introduction

The EMEP network involves co-operation among a large number of participating laboratories, and the quality of the measurements varies among the national data sets. Several different procedures for measuring the main air components, like gaseous SO₂, NO₂, and HNO₃ and particulate SO₄²⁻ and NO₃⁻, have been applied. This has contributed to systematic concentration differences and a comparability problem. Two very important objectives of the EMEP measurement programme are to evaluate trends and validate models. Monitoring of changes in airborne concentrations is a way of evaluating compliance with the Protocols to the Convention of the Long-Range

W. Aas (✉) · J. Schaug · J. E. Hanssen
Norwegian Institute for Air Research,
P.O. Box 100 2027, Kjeller, Norway
e-mail: wenche.aas@nilu.no

Transport of Air Pollutants (LRTAP). To achieve this, it is necessary to have comparable measurements that are independent of methodology, geographical location, temporal resolution and the laboratory used. Quantification of the data quality of EMEP measurements has therefore been an important task for the EMEP Chemical Coordination Centre (CCC). Data quality control consists of several important elements: annual laboratory intercomparison (e.g., Hjellbrekke, Uggerud, Hanssen, & Schaug, 2005), plotting of time series, comparisons of neighbouring measurements sites and so forth. Most important are field intercomparisons that have been carried out regularly since 1985 and enabled one to assess the total measurement differences, including sample preparation, transport, storage, sampling procedures and field and laboratory methods. (e.g., Aas & Hjellbrekke, 2005) Comparing co-located national measurements with a reference is an efficient way of quantifying the overall differences in the data. However, it is difficult to know whether the differences are due to the accuracy of the methods or to operational procedures. In this paper the results from all the field intercomparisons carried out within the EMEP program are used to assess different methodologies and the EMEP measurements in general.

2 Measurements and Data Handling

2.1 Sampling Campaigns

Two large-scale field comparisons for SO_2 and SO_4^{2-} in air were organized by EMEP, at Langenbrügge (DE02) in northern Germany in 1985 (Nodop & Hanssen, 1986) and at Vavihill (SE11) in southern Sweden in 1990 (Semb, Andreasson, Hanssen, Löfblad, & Tykesson, 1991). One large intercomparison for NO_2 was held in Kleiner Feldberg in Germany in 1991 (Fähnrich, Hanssen, & Nodop, 1993). During the second half of the nineties a series of on-site comparisons of national measurements with reference instrumentation have been carried out at several EMEP sites. In order to make the comparison valid for a fairly representative period, it was decided to include measurements over a whole year and about 100 samples. Reference samples were collected one week every month for practical reasons. Results from co-located sampling at seven sites (UK, IE, PT, FR,

DE, PL, CZ) were published in Aas and Semb (2001); additional comparisons at eight other sites (HR, ES, NL, SI, CH, EE, LV and LT) have since then been performed. Furthermore, results from field comparisons of SO_2 performed nationally (DE, TR, AT, FI) were used in the assessment. Some results from these sampling campaigns were presented in the annual EMEP reports on data quality (e.g., Aas & Hjellbrekke, 2005). The site locations and descriptions can be found at the EMEP web pages, <http://www.emep.int>.

2.2 Instrumentation

The reference methods for the EMEP monitoring network are described in the EMEP manual (EMEP, 1996). For SO_2 the reference method is absorption on a potassium hydroxide (KOH) impregnated filter, behind the aerosol filter, which also absorbs other volatile acidic substances such as HNO_3 , and gives solid potassium sulphite and nitrate. Absorption solutions of either hydrogen peroxide or tetrachloromercurate (TCM) are also common methods in EMEP. UV-fluorescence monitors are used at several sites.

The NaI impregnated glass sinter is now the recommended method at background stations with low NO_2 concentrations, and it is suitable when the analysis has to be performed in a laboratory far from the sampling site. The previous recommended method using alkaline absorption solution (like TGS) has a higher detection limit. The Salzmann method used e.g., in Germany and Finland is based on a diazotation reaction in an acidified solution creating a coloured solution that should be measured spectrophotometrically immediately after sampling. The automatic gas-phase chemiluminescence method with a molybdenum converter is also being used at a few sites. For the sum of particulate NO_3 and HNO_3 the filterpack method is used as a reference. In a three-stage filterpack system the first Teflon filter collects aerosols, the second is a Whatman 40 filter impregnated with KOH to collect acid gasses (SO_2 and HNO_3) as described above, and the last is a Whatman 40 filter impregnated with oxalic acid to collect NH_3 . This method makes separation of inorganic nitrogen species in gas and particles biased due to the volatile nature of NH_4NO_3 . Therefore, only the sums of HNO_3 and NO_3^- , and of NH_4^+ and NH_3 are usually given. Total ammonium is not compared in this

paper because a small number of field intercomparisons have included ammonium so far.

2.3 Statistical Tool

The statistical tools used here were developed for the Canadian Air and Precipitation Monitoring Network (CAPMoN) and are described in more details by Sirois and Vet (1999) and EMEP (1996). The precision in the measurements is described by the modified median absolute deviation (M.MAD) (1). M.MAD is a non-parametric estimator of the measurement spread, and it is relatively insensitive to the presence of outliers. M.MAD equals the standard deviation if the underlying frequency is normally distributed multiplying with a factor 1/0.6745. Measurements of this type are however seldom normally distributed and it is therefore common to use the more robust non-parametric statistic to describe the differences. To describe the relative spread we have used the coefficient of variance, CoV (2).

$$\text{M.MAD}(x) = \frac{1}{0.6745} \text{median}(|X_i - \text{median}(x)|) \quad (1)$$

where $x_i = \text{reference}_i - \text{national}_i$

$$\text{CoV} = \frac{\text{M.MAD}}{\text{median}(\text{reference})} * 100\% \quad (2)$$

The systematic errors are estimated using the linear regression slope between the reference (y) and the national sample (x). The regressions were done without a forced zero intercept. This may lead to an over- or underestimation of the biases, but in general the intercepts did not deviate too much from zero, and the slopes did not change radically using either approaches. Outliers were taken out to prevent these from having too much influence on the slope. The reference in the co-located measurement is defined as the measurements performed by CCC, while in the three large-scale campaigns the reference is defined as the average of those using the reference methodology. The reference methods are proven to be accurate and robust; a comparison of several reference samplers showed an uncertainty of less than 10% for all the relevant components (Schaug, Semb, & Hjellbrekke, 1998).

3 Results and Discussion

The comparisons of the average concentrations in the reference and candidate measurements from all the different field intercomparison of SO_2 , NO_2 and SO_4^{2-} are shown in Fig. 1. The statistical results describing the relative precision and bias are given in Fig. 2. The sum of NO_3^- and HNO_3 is not included in the figures since only a few comparisons have been carried out so far.

3.1 SO_2 Measurements

Comparisons of the average concentrations from the different field comparisons of SO_2 show a large concentration span (Fig. 1), and one should notice that the concentration level influence quite a lot on the uncertainty and accuracy of the measurements. Hence the comparison performed in the middle of the 1980 shows much better statistical results than the ones performed in the later years. Low SO_2 concentrations place higher demands on the methods. The summary of all the statistical results is seen in Fig. 2.

The H_2O_2 absorbing solution method gives generally higher concentration than the reference method, Figs. 1 and 2. Of the thirteen comparisons ten sites have a positive bias, the median bias and spread are 16 and 37%, respectively. The problem is highest at low concentration level due to a relatively high detection limit. The detection limits varies between the countries, years and laboratory methods; e.g., in Spain, France and UK the detection limits in 1998 for SO_2 using the H_2O_2 method were 0.5, 0.3 and $0.25 \mu\text{gS/m}^3$, respectively (Aas, Hjellbrekke, & Schaug, 2000). For comparison the reference detection limit was $0.03 \mu\text{gS/m}^3$ (Aas et al., 2000). For the H_2O_2 method this leads too high averages when the concentrations frequently are below $1 \mu\text{gS/m}^3$. In Spain this method doesn't seem to work at all, it is very poor correlation to the reference method. The reason is unknown.

The TCM method usually fails to measure concentrations below $0.5 \mu\text{gS/m}^3$, and in general it also tends to give lower results than the reference method even at higher concentrations. The problems with the method may be due to a chemical interference with oxidants. At some sites the method doesn't work very well (HR04, DE03 and TR01) but at others it seems to be very good (DE09 and DE07). An important

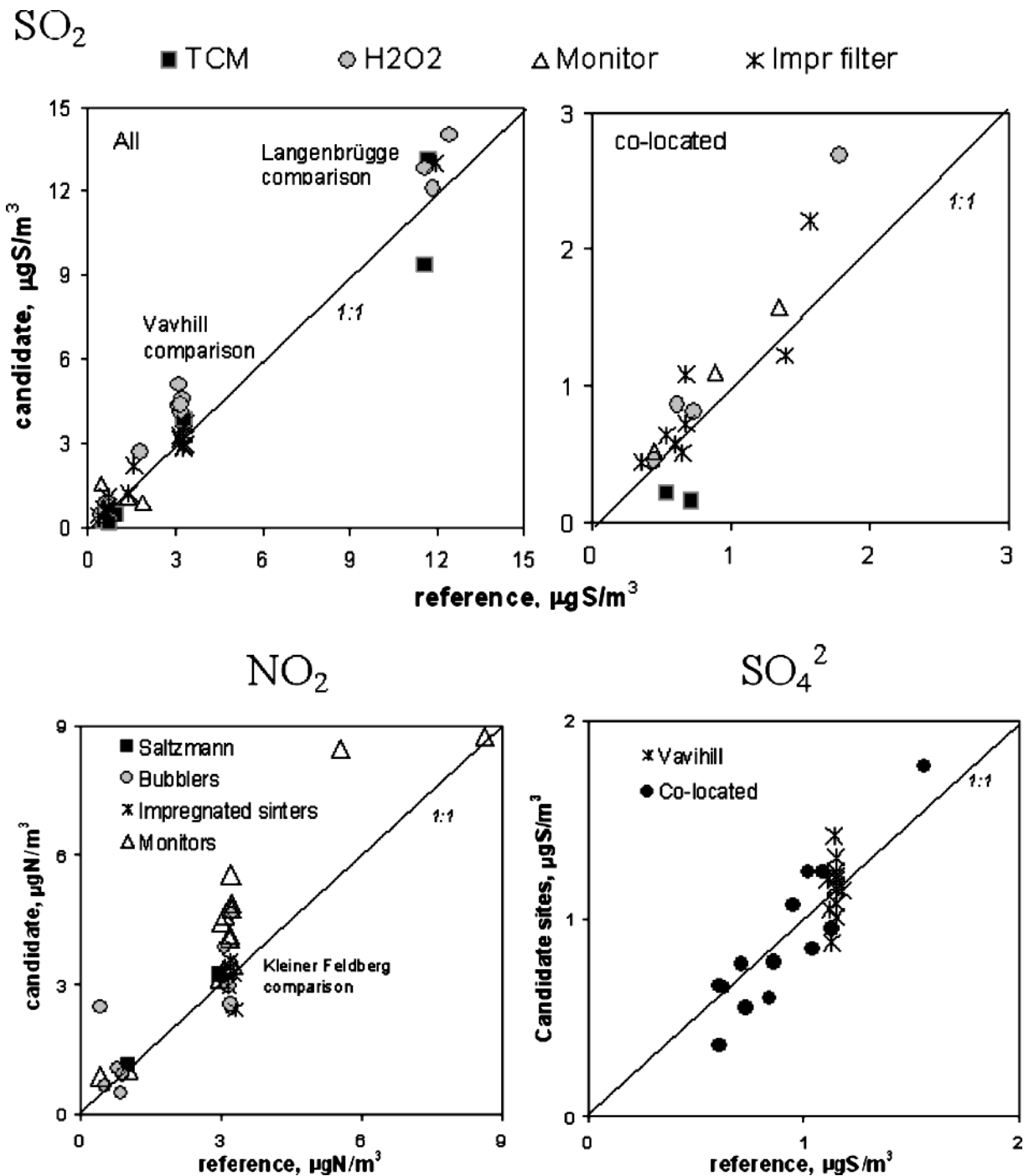


Fig. 1 The correlation between the average concentrations from the reference-and candidate samplers for the comparison of SO_2 , NO_2 and SO_4^{2-} . Data from the large scale field

issue for the TCM method is that the analysis should be done immediately after sampling at the site; this is however not always practically possible since sometimes the samples need to be transported to the

intercomparison are marked out. For SO_2 the *left picture* contains all the comparisons while the *right* includes only those done after 1997 as co-located measurements

laboratory (i.e., in HR and TR). The problems are most severe during the summer, so when using these data for trend analysis it might be wise only to consider the winter data.

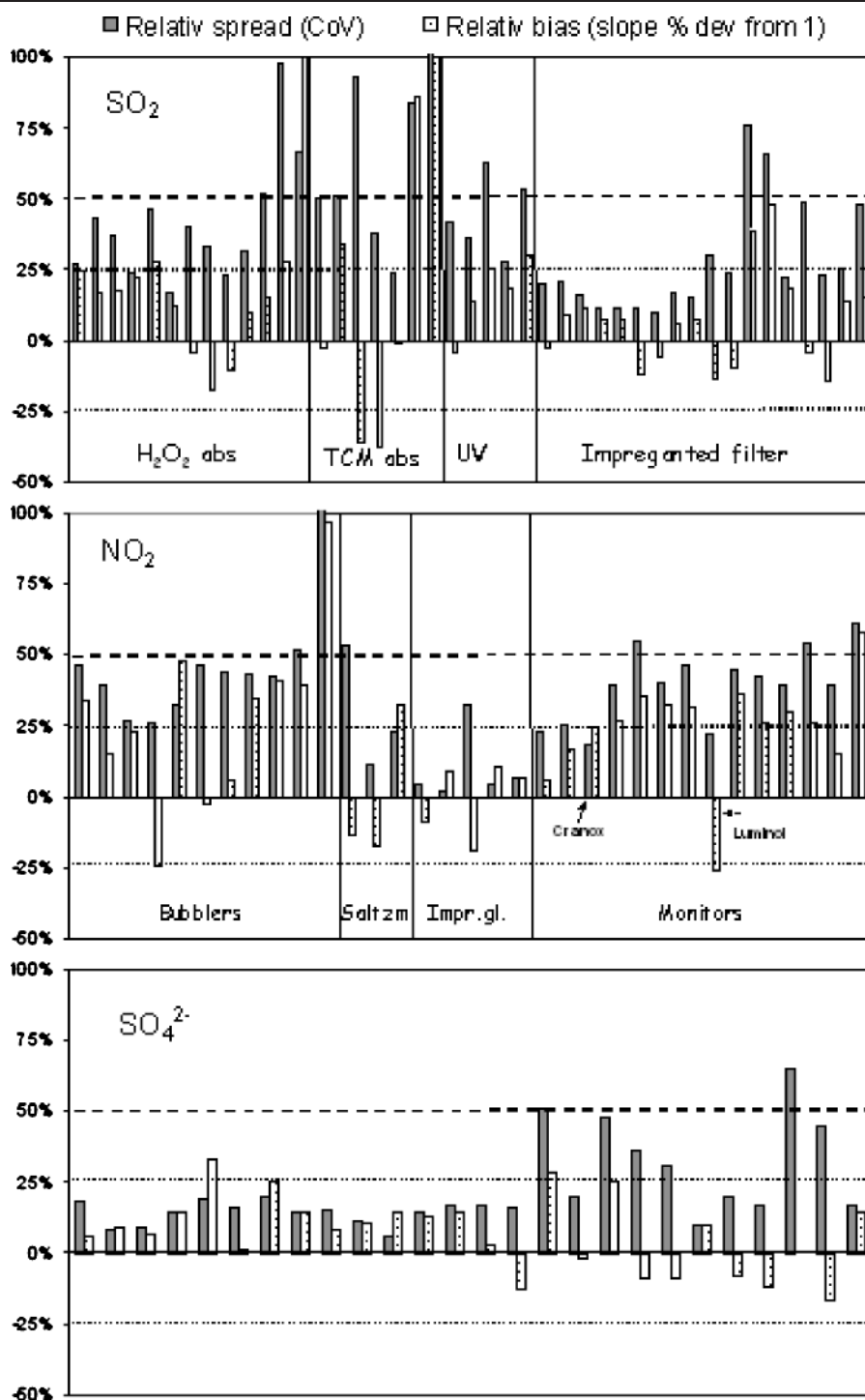


Fig. 2 The relative spread is defined as the coefficients of variance (CoV) and the relative bias as the slope between reference (y) and candidate (x) for SO_2 , NO_2 and SO_4^{2-} . Results

are taken from co-located measurements, large-scale field comparisons, as well as comparisons arranged nationally

The UV fluorescence method shows very varying results. Of the five intercomparisons four of them gives positive bias, and the median bias and spread are 18% and 42% respectively. This method is more demanding than the simple filterpack measurement and it needs frequent maintenance and calibration, the zero-drift can be a significant problem. Interference with NO can be a problem as seen in the comparison in a suburban site in Switzerland (Aas, Hjellbrekke, & Schaugh, 2003), but this should not be a big problem at regional sites. Co-located long-term routine measurements of sulphur dioxide with filter method and fluorescence analyzer at four Finnish EMEP stations (Leppänen, Anttila, Lättilä, & Makkonen, 2005) showed an overall good comparability between the two methods. The best results were achieved in the station most frequently visited and maintained, illustrating that the automatic instruments work best when there are frequent maintenance checks.

The best results are not surprisingly obtained for co-located reference methods, Figs. 1 and 2. Of the 18 comparisons 11 sites have a positive bias, the median bias and spread are 7% and 23 % respectively. But also for this method there are poor results, illustrating that it is necessary to be careful with the QA/QC in all parts of the measurement procedure, and it is not sufficient to rely on a good method only.

3.2 NO₂ Measurements

The alkaline absorption solution gives in general somewhat too high average concentration, and the precision is lower than the reference NaI impregnated glass sinter method. Of the 11 comparisons 9 sites have a positive bias, the median bias and spread are 34% and 43% respectively. For the reference compared with reference methods, the median bias and spread are 6% and 4%. For the Saltzman method, the field comparison at DE03 revealed that this method is not suitable at concentration levels below 1 µg N/m³ (Aas & Semb, 2001), the uncertainty at high concentration levels is also substantial. The results from the chemiluminescence monitors are variable. In general the monitors tend to overestimate the concentration level, of the 14 comparisons 12 sites have a positive bias, the median bias and spread are 26 and 40%, respectively. The zero-drift may be a main problem at some sites. The method can be as sensitive as the NaI method; however, the monitor is not

specific because other reducible nitrogen compounds (e.g., HNO₃ and PAN) give a positive interference, which can be a serious problem at some sites. If a monitor is being used it is recommended to have a photolytic converter like the Cranox instrument. As for the SO₂ monitor, frequent maintenance is also a necessity for the chemiluminescence monitor to ensure accurate measurements.

3.3 Particulate SO₄²⁻ and NO₃⁻+HNO₃ Measurements

Particulate sulphate is much easier to sample than the gases discussed above because of few interference problems, and the detection limit is mainly determined by the lab method. The results from the comparisons also show that (Fig. 2). But there are laboratories that need improvements in their quality assurance system. Only a few comparison results have been obtained so far for the sum of nitric acid and nitrate in particles, these indicate however, that systematic differences may occur and correction for field blanks can be an important issue regarding these differences.

4 Conclusion

Field intercomparison has proven to be highly useful to document method performance and the quality of EMEP measurements. Evaluation of trends particularly requires consistent data as well as for documentation of methods and the effects of changes in methods, equipment and procedures. Ideally, methods should not be changed. However, when equipment must be renewed, procedures are likely to be changed. It is therefore important that the methods and sampling protocols are documented and defined in such a way that the effect of changes can be assessed and tested under representative conditions. Filterpack method for main components (i.e., SO₂, SO₄²⁻ and NO₃⁻+HNO₃) in air and NaI impregnated sinters for NO₂ are the best available methods at rural sites. These methods give reliable and sensible results at low concentration levels and practical experience with these methods now goes back more than 20 years. However, other methods are also useful and can be of the same quality and comparable in several cases. In addition, using a reference method is not a guaranty for good data quality, the sampling protocols in lab and field have to be followed closely, and regular

field- and laboratory intercomparison are necessary to check the performance of the measurements.

Acknowledgement The EMEP program (UN-ECE) has financed most of this work. In addition, several laboratories have contributed with their results. Their work and willingness to cooperate and share their results are highly appreciated.

References

- Aas, W., & Hjellbrekke, A.-G. (2005). *Data quality 2003. Quality assurance and field intercomparison*. Kjeller, Norwegian Institute for Air Research. EMEP/CCC-Report 6/2005.
- Aas, W., Hjellbrekke, A.-G., & Schaugh, J. (2000). *Data quality 1998, quality assurance and field intercomparison*. Kjeller, Norwegian Institute for Air Research. EMEP/CCC-Report 6/2000.
- Aas, W., Hjellbrekke, A.-G., & Schaugh, J. (2003). *Data quality 2002. Quality assurance and field intercomparison*. Kjeller, Norwegian Institute for Air Research. EMEP/CCC-Report 6/2003.
- Aas, W., & Semb, A. (2001). Standardisation of methods for long-term monitoring. *Water, Air and Soil Pollution*, 130, 1596–1600.
- EMEP. (1996). *Manual for sampling and chemical analysis*. Revised Nov. 2001. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 1/95). URL: <http://www.nilu.no/projects/ccc/manual/index.html>.
- Fährnich, B., Hanssen, J. E., & Nodop, K. (1993). *Comparison of measuring methods for nitrogen dioxide in ambient air*. Kleiner Feldberg, Federal Republic of Germany 21st April to 31st May 1991. Lillestrøm, Norwegian Institute for Air Research (EMEP/CCC-Report 3/93).
- Hjellbrekke, A.-G., Uggerud, H. T., Hanssen, J. E., & Schaugh, J. (2005). *The twenty-second intercomparison of analytical methods within EMEP*. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/2005).
- Leppänen, S., Anttila, P., Lättälä, H., & Makkonen, U. (2005). Long-term comparison of filter method and sensitive analyser in monitoring of sulphur dioxide. *Atmospheric Environment*, 39, 14, 2683–2693.
- Nodop, K., & Hanssen, J. E. (1986). *Field intercomparison of measuring methods for sulphur dioxide and particulate sulphate in ambient air*. Langenbrügge, Federal Republic of Germany, 7th November 1985 to 24th January 1986. Lillestrøm, Norwegian Institute for Air Research (EMEP/CCC-Report 2/86).
- Schaugh, J., Semb, A., & Hjellbrekke, A.-G. (1998). *Data quality 1996, quality assurance and field intercomparison*. Kjeller, Norwegian Institute for Air Research. EMEP/CCC-Report 6/1998.
- Semb, A., Andreasson, K., Hanssen, J. E., Lövblad, G., & Tykesson, A. (1991). *Vavihill, field intercomparison of samplers for sulphur dioxide and sulphate in air*. Lillestrøm, Norwegian Institute of Air Research (EMEP/CCC Report 4/91).
- Sirois, A., & Vet, R. (1999). The precision of precipitation chemistry measurements in the Canadian air and precipitation monitoring network (CAPMoN). *Environmental Monitoring and Assessment*, 57, 301–329.

Variations in the Fluoride Level in Precipitation in a Region of Human Impact

Barbara Walna · Iwona Kurzyca · Jerzy Siepak

Received: 17 June 2005 / Accepted: 14 January 2006 / Published online: 6 January 2007
© Springer Science + Business Media B.V. 2007

Abstract The research concerns the Wielkopolski National Park (West Poland), which suffered a huge human impact in the 1970s and 1980s owing to the nearby location of an industrial plant. Since then, fundamental technological changes that it introduced into its production of phosphate fertilizers have radically reduced the amount of pollution emitted. A three-year study (2002–2004) of fluorides in precipitation in open terrain and under tree crowns showed their concentrations to range from levels below the detection limit (0.003 mg/l) to 0.560 mg/l. Those registered under tree crowns were several times higher and indicated substantial dry deposition of fluorides on the trees. The highest values were recorded in 2003, with 43% of samples ranging from 0.01 to 0.05 mg/l, and with 51% of throughfall ranging from 0.10 to 0.50 mg/l. A strong connection was shown to exist between fluoride and sulphate concentrations in the precipitation. An analysis was made of the available data on F concentrations in the

air and the dust levels around the factory, but these figures did not show an unequivocal effect on F concentrations in precipitation. A great similarity was found to occur between the fluoride content in rainwater in the Wielkopolski National Park and in the centre of the nearby Poznań metropolitan area, which indicates that there are also other F sources besides the local factory.

Keywords fluoride · Poznań · precipitation · throughfall · the Wielkopolski National Park

1 Introduction

Fluorine is a widespread component of the Earth's crust, but air pollution with its compounds are not common and usually occurs at a local scale in the form of industrial emissions. They contain both particulate and gaseous forms of fluorine. The former are particles of various sizes and chemical composition containing fluorapatite, cryolite, or fluorite. They are deposited on leaf surfaces and their penetration inside depends on their solubility. Predominant among the gaseous forms is hydrogen fluoride (HF). It has the greatest impact on the vegetation, closely followed by silicon tetrafluoride (SiF₄), fluosilicic acid (H₂SiF₆), and free fluorine F₂ (Zimmermann et al., 2003). Both gaseous and particulate pollution can dissolve on contact with water

B. Walna (✉)
Jeziory Ecological Station, Adam Mickiewicz University,
62-050 Mosina P. O. Box 40, Poland
e-mail: walna@amu.edu.pl

I. Kurzyca · J. Siepak
Department of Water and Soil Analysis,
Adam Mickiewicz University,
24 Drzymały Str.,
60-613 Poznań, Poland

vapour or rain drops and get inside plants, chiefly through stomata in the leaves. Fluorine which has penetrated into a plant tissue affects its metabolism in a number of ways (Feng, Ogura, Feng, Zhang, & Shimizu, 2003). One of the major effects is reduced photosynthetic activity, as well as inhibition of enzymatic activity (Karolewski, Siepak, & Gramowska, 2000). The changes also involve the ultrastructure and chlorophyll content (Klumpp, Domingos, & Klumpp, 1996). The kind of damage depends on the species and age of plants. Symptoms include chlorosis or even necrosis of leaves (Weinstein, 1977; Karolewski et al., 2000). Permanent stress caused by industrial sources also has wider ecological consequences: it alters the structure and composition of plant communities and makes fluorine enter other links of the trophic network (McCune & Weinstein, 2002). In areas subject to fluorine emissions adverse effects have been observed in the bone system of both animals and humans. One should also note the behaviour of fluorine in the soil (Horner & Bell, 1995; Pickering, 1985). It forms many complex ions (AlF^{2+} , AlF^{4-}) which start to migrate and a substantial proportion of them enter groundwater (Saether, Andreassen, & Semb, 1995). The soils in regions affected by fluorine emissions display an accumulation of this element (Horntvedt, 1995; Arnesen, Abrahamsen, Sandvik, & Krogstad, 1995). In fluorine-contaminated soils the content of organic matter declines, and so does the activity of microorganisms (van Wensem & Adena, 1991).

In spite of the great interest in the effects of fluorine on the growth and development of plants and other organisms, the number of articles describing fluorine content in precipitation is small, and in areas where F emission is not suspected the study is not included in a monitoring programme.

The aim of the present research was to determine the content of fluorides in precipitation collected in a protected area, but still one experiencing some human impact, and to establish where the rainwater contaminants come from.

2 Experimental

2.1 Site Description

Rainwater samples were collected at the Jeziory Ecological Station of Adam Mickiewicz University

situated in the woodland area of the Wielkopolski National Park (west-central Poland). This location would seem to ensure some isolation from the pollution of the nearby (25 km) large metropolitan area of Poznań (ca. 600,000 inhabitants). There are a host of bigger and smaller industrial plants in the city, some of which emit fluorine compounds. Additionally, between the city and the rainwater collection site in the Park, at a distance of about 12 km, there is a large Luboń Chemical Works which has for years been manufacturing phosphate fertilizers, hydrofluoric acid, and sulphuric acid. Many pro-ecological measures taken by the plant over the last 15 years have limited its environmental nuisance considerably; still, the production carried out on a cyclic basis remains undoubtedly a source of pollution of the atmospheric air. To characterise the previous environmental impact of the works, let us quote its emission figures concerning fluorine compounds: 1988 – 19.5 Mg/year, 1989 – 18.2 Mg/year, 1990 – 6.2 Mg/year, while in the following years emission levels were maintained at about 1.5 Mg/year (M. Górecka, personal communication). This is a considerable ecological success accomplished through a limitation of the production of sulphuric acid, powdered superphosphate and hydrofluoric acid, and a change in technology.

2.2 Materials and Methods

At the Jeziory Ecological Station a detailed chemical analysis of precipitation is carried out on a daily basis. The present analysis covered all the samples collected in 2002, 2003 and 2004, that is, 174 samples of rainwater collected in open terrain and 132 from under trees (about 50-year-old oaks). To collect precipitation, use is made of plastic funnels 56 cm in diameter placed at an altitude of 1 m. The amount of rainwater is determined manually using a Hellmann rain gauge. As soon as a sample is collected its pH and electrical conductivity are determined. Fluorides (and other ions) were determined with the help of ion chromatography (DIONEX 120) after filtered with a pore diameter of 0.45 μm . A detailed description of the experimental methods, their calibration and validation can be found elsewhere (Walna, Kurzyca, & Siepak, 2004; Polkowska et al., 2005). To test the correctness of performed analyses, certified reference material was also analyzed. The CRM was a low-pH acid rain sample from

southern Ontario (Canada), RAIN-97, whose composition resembled that of precipitation under study.

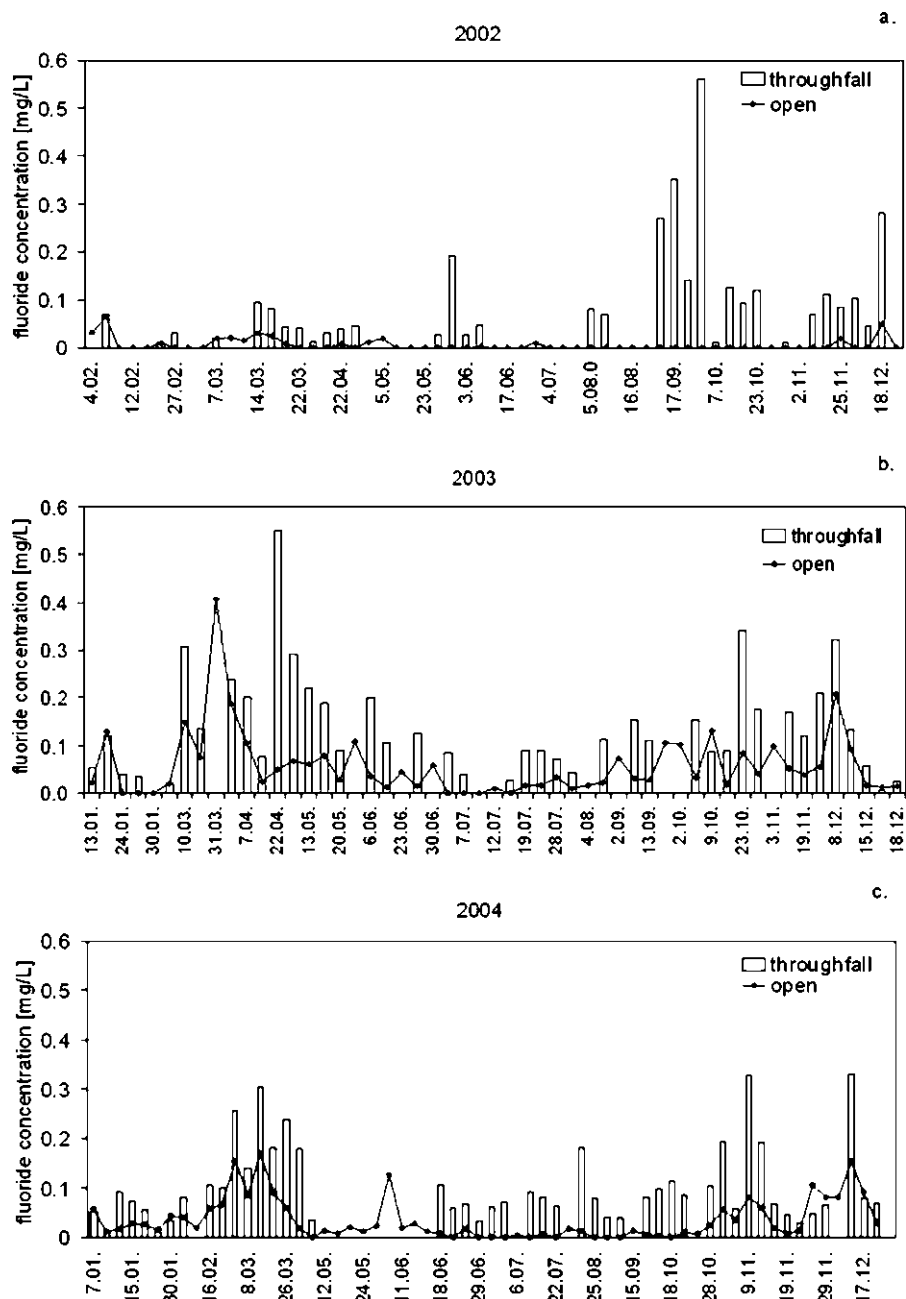
It can be noticed that the number of throughfall samples was smaller. This follows from the fact that in the summer, when rainfall is low, its entire amount stays on leaves or evaporates. Another reason is the elimination from the analysis of some samples contaminated with organic remains during the blooming of trees.

Fig. 1 Fluoride concentrations in precipitation in open terrain and throughfall in 2002, 2003 and 2004. The uncertainty of all measurements expressed as RSD did not exceed 12%

3 Results and Discussion

Figure 1a, b and c show annual patterns of fluoride concentrations in open terrain and under trees over the years 2002–2004, while Table 1 presents fluoride levels in the particular years.

The analysed years differ markedly. The year 2003, in which the annual rainfall recorded (338 mm) was much lower than the multi-year average (550 mm),



had an annual fluoride concentration in open terrain ten times higher than the year 2002 (639 mm), when most samples displayed a fluoride level below the detection limit (0.003 mg/l). The maximum 2003 figures were also several times higher than the maximum 2002 ones. For all the cases, the rainwater collected under trees was much richer in fluorides than the respective open-terrain samples. In 2002 one could observe on many occasions that minimum fluoride levels in open-terrain precipitation corresponded to great concentrations in the throughfall (e.g., the August–October period). This fact indicates dry deposition to have a decisive share in the total deposition of fluorine. The differences in the mean annual throughfall concentrations were not as wide as those in open terrain. This is indicative of similar proportions of particulates and different proportions of gaseous pollutants in those years. What characterised the years 2003 and 2004 was that the range of F concentrations in a considerable number of rainwater samples (43%) was 0.010–0.050 mg/l. In turn, the precipitation collected under trees differed markedly: in 2003 most rainwater (51% of samples) had concentrations one order of magnitude higher, between 0.100 and 0.500 mg/l, while in 2004 they ranged from 0.050 to 0.100 mg/l (45% of samples). The deposition of fluorides in 2003 (12.15 mg/m²/year) was eight times higher than in 2002 (1.67 mg/m²/year), while in 2004 was slightly smaller, at 8.63 mg/m²/year, with a rainfall total of 431 mm.

When studying the annual patterns of fluoride concentrations in the particular years, one can notice a regularity: an increase in the concentrations in both,

open-terrain and throughfall rainwater in the spring and autumn/winter seasons. Their corresponding highest fluoride levels were: 0.560 mg/l – 30 Sept. 2002 (throughfall) – Fig. 1a, 0.406 mg/l – 30 March 2003 (open) and 0.550 mg/l – 22 April 2003 (throughfall) – Fig. 1b, 0.330 mg/l – 9 Nov. 2004 and 15 Dec. 2004 (throughfall) – Fig. 1c.

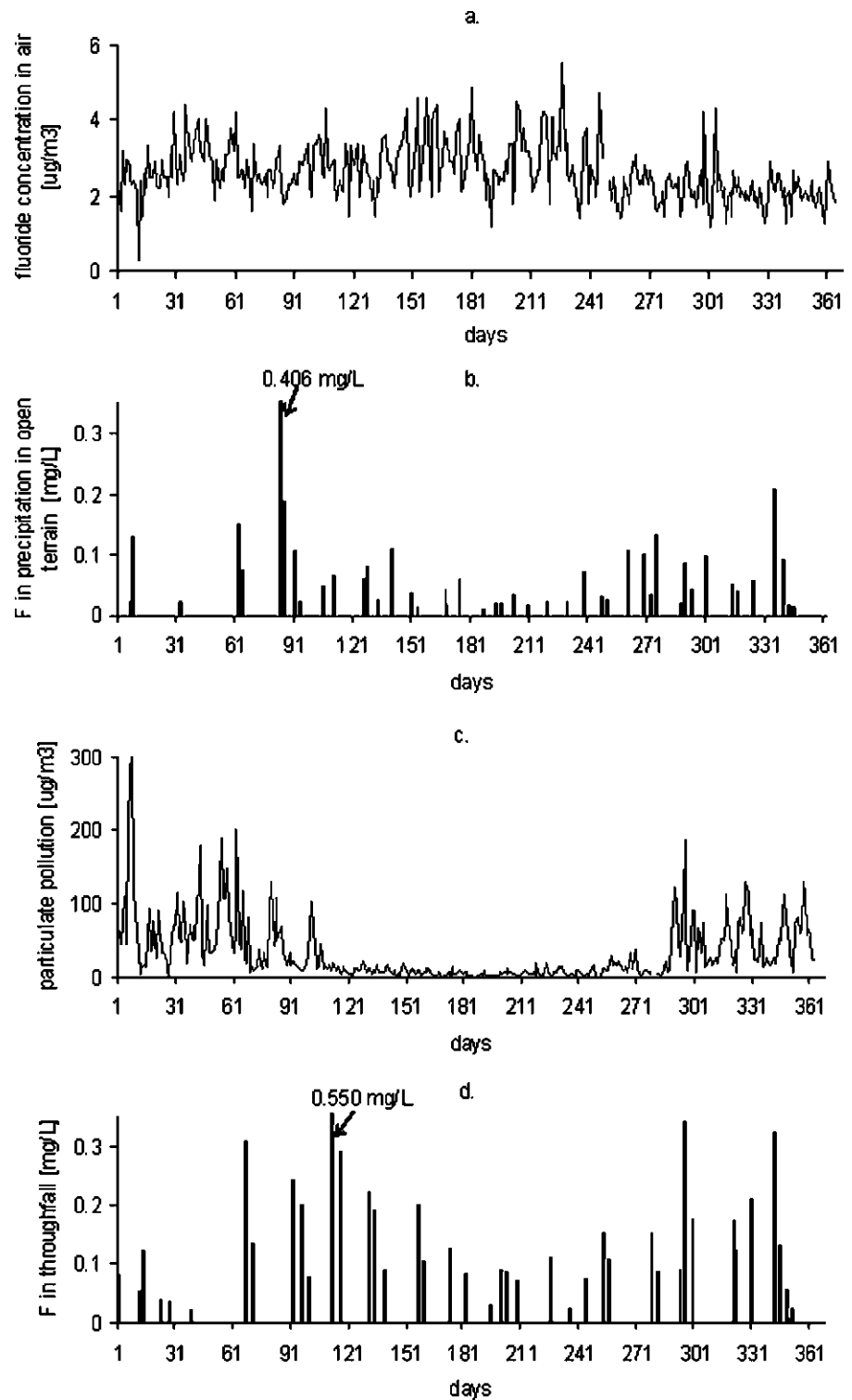
Unfortunately, no monitoring studies of the fluoride content in precipitation in the area were made before the period described in the present results. Still, a few checks on fluoride levels conducted in the years 1996–1999 revealed incidences of considerable concentrations (max. 0.69 mg/l) (Walna & Siepak, 1999). Over the present study period, 2002–2004, the mean annual pH was equal to 4.28, and a detailed analysis of the anion composition showed the presence of four basic anions at the following concentrations: SO_4^{2-} – 35%, NO_3^- – 17%, Cl^- – 47%, and F^- – 1%. The low pH of the precipitation accompanied by a high content of sulphate and nitrate ions has an interactive effect on the vegetation and soil: it affects the ecological properties of plant species and brings about an instability of the ecosystem (Fangmeier, Bender, Weigl, & Jager, 2002). When analysing non-fluoride contaminants in the precipitation, one can observe simultaneous maximum concentrations and similar annual patterns of sulphates and nitrates (Walna et al. 2004). By calculating coefficients of the correlation, it was possible to estimate the similarity of the variation curves and to suspect a common source of some contaminants (Table 1). The highest correlation between sulphate and fluoride ions and for nitrate

Table 1 Annual characteristics and correlation coefficients ($p < 0.05$) for rainfall in the open terrain and in throughfall in 2002, 2003 and 2004

Annual characteristics	2002		2003		2004	
	Open	Throughfall	Open	Throughfall	Open	Throughfall
Average conc. $\pm$ SD (mg/l)	0.006 $\pm$ 0.012	0.077 $\pm$ 0.111	0.057 $\pm$ 0.069	0.133 $\pm$ 0.109	0.035 $\pm$ 0.042	0.103 $\pm$ 0.080
Concentration range (mg/l)	0.003*–0.064	0.003*–0.560	0.003*–0.406	0.003*–0.550	0.003*–0.170	0.003*–0.330
Number of samples	59	41	53	43	62	48
Correlation coefficient r SO_4/F	0.48	0.61	0.89	0.77	0.74	0.75
Correlation coefficient r NO_3/F	0.39	0.64	0.79	0.72	0.72	0.40
Correlation coefficient r Cl/F	0.29	0.32	0.52	0.57	0.53	0.45
Correlation coefficient r Ca/F	0.24	0.39	0.56	0.54	0.32	0.53
Correlation coefficient r Na/F	0.22	0.12	0.72	0.34	0.26	0.11

* Detection limit

Fig. 2 Particulate and fluoride concentrations in the air in comparison with fluoride in precipitation and throughfall (2003)



and fluoride ions in 2003 was calculated. No correlation was found to occur between the amount of rainfall and H^+ concentrations which indicate that owing to their insignificant proportion (1%), fluorides do not affect the level of rain acidification in any crucial way. Also the amount of rainfall does not display a simple relation to F concentrations in rainwater. The high correlation between the levels of F and sulphates and nitrates may suggest a similar source of pollution. The big phosphate fertiliser works in the vicinity comes to mind as a possible source.

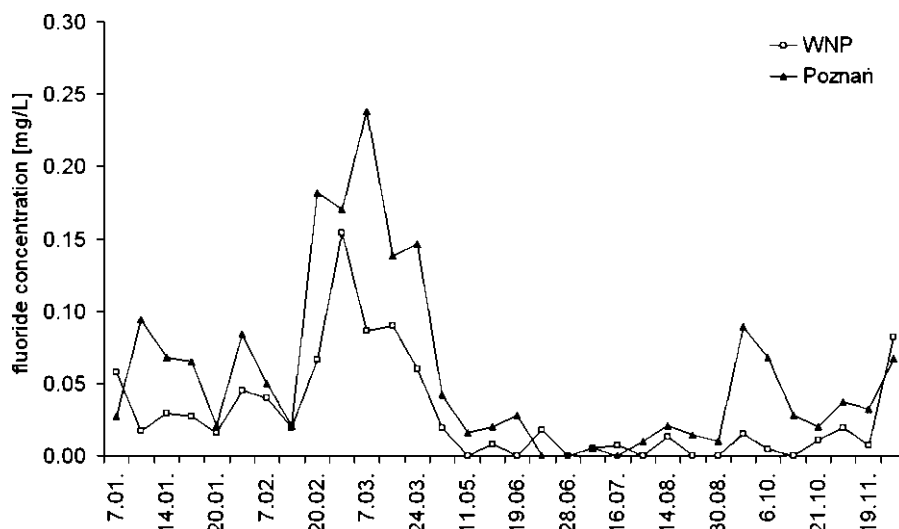
In order to corroborate this hypothesis, the results were examined of the monitoring studies of F and particulates in the air made for environmental control purposes by the plant (in-house materials). The data were collected on a daily basis at three points located around the plant at a distance of some 3 km. The results for 2003, when the highest fluoride pollution levels were recorded in precipitation, are presented in Fig. 2. Figure 2c shows a typical pattern of the dust level with a minimum in the summer. Some correlation between dustiness and F content in precipitation can be traced in March, when on the seventh a fairly high dust level of $117 \mu\text{g}/\text{m}^3$ was recorded followed on the next days by a fall of rain with substantial F concentrations both in open terrain ($0.149 \text{ mg}/\text{l}$) and in throughfall ($0.307 \text{ mg}/\text{l}$), while dustiness dropped to $19 \mu\text{g}/\text{m}^3$. However, the next rainfall events with considerable F levels were not correlated with high dustiness figures. The next high fluorine concentration in throughfall on 23 Oct. 2003 ($0.341 \text{ mg}/\text{l}$) co-occurred with a high dust level of $188 \mu\text{g}/\text{m}^3$, but it is

also possible to find examples of high F levels in rainwater corresponding to low levels of dust, e.g. 8 Dec. 2003 with $0.323 \text{ mg}/\text{l}$ (F) and $26 \mu\text{g}/\text{m}^3$ (dust), or 10 Sept. 2003 with $0.154 \text{ mg}/\text{l}$ (F) and $10 \mu\text{g}/\text{m}^3$ (dust).

A search for a relation between F levels in precipitation and in the air at the control stations is equally inconclusive (Fig. 2c). In 2003 the concentration of F in the air was similar to the 2002 figure and did not show the anticipated variation connected with the seasonal increase in production. The mean annual F concentration for the three sites around the works were 2.2 , 2.6 and $3.1 \mu\text{g}/\text{m}^3$ (with the standard set at $2.0 \mu\text{g}/\text{m}^3$), while the maximum figures were 4.1 , 5.5 and $7.3 \mu\text{g}/\text{m}^3$, respectively. Thus, the presented diagram did not provide a basis for the explanation of the substantial concentrations over the study period. Neither did it indicate in an unambiguous way the source polluting the precipitation. It should be remembered, however, that the lowest concentrations that produce visible injury are around $0.3 \mu\text{g}/\text{m}^3$ if exposure time is sufficiently long (Cape, Fowler, & Davison, 2003).

In seeking the source of rainwater contamination with fluorides, a comparison was made between their levels in precipitation collected in the WNP and in the centre of Poznań. Those rainfall events were chosen that were simultaneous or followed each other closely. For illustration, they are presented in a common diagram (Fig. 3). Its most characteristic feature is the striking similarity of the F concentrations recorded at these two locations, so totally different in terms of the human

Fig. 3 Comparison of F concentrations in precipitation at two sites – the Wielkopolski National Park (WNP) and Poznań (city) in 2004. The uncertainty of all measurements expressed as RSD did not exceed 12%



impact. There are only three rainfall events when the WNP figures are somewhat higher than the Poznań ones, but the differences are slight. In the February–May period of 2004 there is a distinct maximum with a highly similar shape for the two locations. The correlation coefficient for them is high, 0.78. Curves of an equally highly similar shape were also obtained for 2003. There were then only four precipitation events in the Park, in March and April that exceeded the F levels in Poznań. After those dates the curves follow a similar pattern, which is corroborated by the correlation coefficient, 0.84. It may also be added that the maximum F figures in the WNP and Poznań co-occur with exceptionally high concentrations of Cl^- , NO_3^- and SO_4^{2-} (Walna et al., 2004).

When comparing the above results with the data from literature, one can state that the mean F concentration in the 2003 and 2004 precipitation was more than twice as high as that obtained for southern Norway, 0.020 mg/l (Saether et al., 1995). In Norway the F/SO_4 and F/NO_3 correlation coefficients were similar to those obtained in the present research. According to the literature, the probable background level of fluorides in precipitation is 2–20 $\mu\text{g}/\text{l}$ with a mean of 8 $\mu\text{g}/\text{l}$ (Barnard & Nordstrom, 1982). Our results, with the exception of 2002, greatly exceed those figures, which is indicative of a strong impact of human-generated pollution. However, the calculated fluoride input in 2003 was one-sixth of that obtained for southern Saxony (the Black Triangle) in 1998 (Zimmermann et al., 2003), where the F input played a major role in explaining forest decline phenomena. In turn, typical F concentrations in Dutch rainwater (van den Hoop, Cleven, van Staden, & Neele, 1996) were found to be in the same range as in our study in 2002. Studies quoted for a variety of locations in the world (Feng et al., 2003) show China to be the country with the highest F concentrations in wet deposition, while the world mean given above is close to the average obtained in our study for precipitation in 2003.

4 Conclusions

The three-year study (2002–2004) of fluoride levels in precipitation has revealed their considerable concentrations in rainwater, especially under tree crowns, despite a serious reduction in industrial emissions. A strong connection between fluoride and sulphate

concentrations in the precipitation may indicate a common source of pollution. An analysis of the available data on F concentrations in the air and dustiness does not unequivocally confirm the suspected origin of the pollutants. The unexpected great similarity between the results for the Wielkopolski National Park and the centre of the Poznań metropolitan area suggests a search for additional sources of fluorine emission employing air mass back trajectory analysis and other climatic parameters.

The strong effect of fluorides on the biotic elements of the environment, and its serious consequences in a poorly buffered soil with high acid deposition call for a permanent monitoring of their deposition.

References

- Arnesen, A. K. M. G., Abrahamsen, G., Sandvik, G., & Krogstad, T. (1995). Al smelters and fluoride pollution of soil and soil solution in Norway. *Science of the Total Environment*, 163, 39–53.
- Barnard, W. R., & Nordstrom, D. K. (1982). Fluoride in precipitation. II. Implications for the geochemical cycling of fluorine. *Atmospheric Environment*, 16(1), 105–111.
- Cape, J. N., Fowler, D., & Davison, A. (2003). Ecological effects of sulfur dioxide, fluorides and minor air pollutants: Recent trends and research needs. *Environment International*, 29, 201–211.
- Fangmeier, A., Bender, J., Weigl, H. J., & Jager, H. J. (2002). Impact of mixture pollutants. In J. N. B. Bell & M. Treshow (Eds.), *Air pollution and plant life* (pp. 279–298). New York: Wiley.
- Feng, Y. W., Ogura, N., Feng, Z. W., Zhang, F. Z., & Shimizu, H. (2003). The concentration and sources of fluoride in atmospheric depositions in Beijing, China. *Water, Air, & Soil Pollution*, 145, 95–107.
- Horner, J. M., & Bell, J. N. B. (1995). Effects of fluoride and acidity on early plant growth. *Agriculture, Ecosystems and Environment*, 52, 205–211.
- Horntvedt, R. (1995). Fluoride uptake in conifers related to emissions from aluminium smelters in Norway. *Science of the Total Environment*, 163, 35–37.
- Karolewski, P., Siepak, J., & Gramowska, H. (2000). Response of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea Abies*) and Douglas fir (*Pseudotsuga menziesii*) needles to environment pollution with fluorine compounds. *Dendrobiology*, 45, 41–46.
- Klumpp, A., Domingos, M., & Klumpp, G. (1996). Assessment of the vegetation risk by fluoride emissions from fertilizer industries at Cubatao, Brazil. *Science of the Total Environment*, 192, 219–228.
- McCune, D. C., & Weinstein, L. H. (2002). Impact of fluoride. In J. N. B. Bell & M. Treshow (Eds.), *Air pollution and plant life* (pp. 181–190). New York: Wiley.
- Pickering, W. F. (1985). The mobility of soluble fluoride in soils. *Environmental Pollution*, 9, 281–308.

- Polkowska, Ź., Astel, A., Walna, B., Małek, S., Mędrzycka, K., Górecki, T., et al. (2005). Chemical composition of rainwater and throughfall – A four year series from three different sampling sites in Poland. *Atmospheric Environment*, 39, 837–855.
- Saether, O. M., Andreassen, B. T., & Semb, A. (1995). Amounts and sources of fluoride in precipitation over southern Norway. *Atmospheric Environment*, 29(15), 1785–1793.
- Van den Hoop, M. A. G. T., Cleven, R. F. M. J., van Staden, J. J., & Neele, J. (1996). Analysis of fluoride in rain water. Comparison of capillary electrophoresis with ion chromatography and ion selective electrode potentiometry. *Chromatography A*, 739, 241–248.
- Van Wensem, J., & Adena, T. (1991). Effects of fluoride on soil fauna mediated litter decomposition. *Environmental Pollution*, 46, 1–9.
- Walna, B., Kurzyca, I., & Siepak, J. (2004). Local effects of pollution on chemical composition of precipitation in areas differing in human impact. *Polish Journal of Environmental Studies*, 13, 36–42.
- Walna, B., & Siepak, J. (1999). Research on the variability of physical-chemical parameters characterizing acidic atmospheric precipitation at the Jeziory Ecological Station in the Wielkopolski National Park (Poland). *Science of the Total Environment*, 239, 173–187.
- Weinstein, L. H. (1977). Fluoride and plant life. *Journal of Occupational Medicine*, 19, 49–78.
- Zimmermann, F., Lux, H., Maenhaut, W., Matschullat, J., Plessow, K., Reuter, F., et al. (2003). A review of air pollution and atmospheric deposition dynamics in southern Saxony, Germany, Central Europe. *Atmospheric Environment*, 37, 671–691.

Long Term Trends in Sulphur and Nitrogen Deposition in Europe and the Cause of Non-linearities

David Fowler · Rognvald Smith · Jennifer Muller ·
John Neil Cape · Mark Sutton ·
Jan Willem Erisman · Hilde Fagerli

Received: 17 June 2005 / Accepted: 14 January 2006 / Published online: 16 February 2007
© Springer Science + Business Media B.V. 2007

Abstract Emissions of sulphur and oxidized nitrogen compounds in Europe have been reduced following a series of control measures during the last two decades. These changes have taken place during a period in which the primary gases and the wet deposition throughout Europe were extensively monitored. Since the end of the 1970s, for example land based sulphur emissions declined by between 90 and 70% depending on the region. Over the same period the total deposition of sulphur and its partitioning into wet and dry deposition have declined, but the spatial pattern in the reduction in deposition differs from that of emission and has changed with time. Such non-linearities in the emission-deposition relationship are important to understand as they complicate the process of assessing the effects of emission reduction strategies. Observed non-linearities in terrestrial sulphur emission-deposition patterns have been identi-

fied in north west Europe due to increases in marine emissions, and are currently slowing the recovery of freshwater ecosystems. Changes in the relative amounts of SO₂ and NH₃ in air over the last two decades have also changed the affinity of terrestrial surfaces for SO₂ and have therefore changed the deposition velocity of SO₂ over substantial areas. The consequence of this effect has been the very rapid reduction in ambient SO₂ concentration in some of the major source areas of Europe, where NH₃ did not change much. Interactions between the different pollutants, generating non-linearities are now being incorporated in long-range transport models to simulate the effects of historical emission trends and to provide projections into the future. This paper identifies non-linearities in emission deposition relationships for sulphur and nitrogen compounds in Europe using data from the EMEP long-rang transport model and measured concentration fields of the major ions in precipitation and of SO₂ and NO₂ in surface air.

D. Fowler (✉) · R. Smith · J. Muller · J. N. Cape ·
M. Sutton
Centre for Ecology and Hydrology, Bush Estate,
Edinburgh, Scotland EH26 0QB, UK
e-mail: dfo@ceh.ac.uk

J. W. Erisman
Energy research Centre of The Netherlands,
P.O.Box 1, 1755 ZG Petten, The Netherlands

H. Fagerli
Norwegian Meteorological Institute,
P.O. Box 43, Blindern, 0313 Oslo, Norway

Keywords nitrogen · non-linearity · shipping ·
sulphur · wet and dry deposition

1 Introduction

The control of acidifying pollutant emissions in Europe has progressed steadily since the early 1980s, when the first steps to control sulphur emissions were introduced

(Brydges & Wilson, 1991). The main focus of the early control measures was sulphur, as the major contributor to acidification of terrestrial ecosystems in Europe (Johnson & Reuss, 1984). Following these early steps in the process, emission controls were extended to nitrogen compounds, with a clear focus on oxidized nitrogen and to volatile organic compounds (VOC) to broaden the control strategy from acidification to include ground level ozone. The most recent UNECE Protocol (Gothenburg) and related Directives from the European Commission extended the degree of control of emissions leading to acidification and included eutrophication and ground level ozone and includes targets for NH_3 . An up to date summary of the control measures in Europe and emerging air quality issues is provided by Grennfelt and Hov (2005). The reductions in pollutant emissions vary considerably in time and space throughout Europe, furthermore the extent of the controls on the different pollutants varied greatly, with very large reductions in emissions of SO_2 but only modest reductions in NH_3 emissions. The pollutants concerned are all reactive in the atmosphere, and differential reductions in emissions have the potential to cause changes in the source-receptor relationships with time, due for example to changes in the chemical processing and deposition of individual pollutants. Improvements in air quality may therefore be more variable spatially than expected on the basis of a strictly linear decline in deposition with a constant spatial pattern in deposition following emission reductions.

In the case of sulphur, emitted in the gaseous state as SO_2 , the oxidation occurs either in the gas phase through reaction with OH or by heterogeneous processes in clouds or in aerosols and in this case the pH of the droplet strongly influences the reaction pathway and the preferred oxidant. The most important base regulating the acidity of cloud droplets over Europe is NH_3 , thus emissions of NH_3 have the potential to regulate the oxidation pathway of SO_2 (Wayne, 1985) and therewith the transport distance of SO_2 .

Non-linearities may also occur through changes in the terrestrial sink for key pollutants with time. In the case of SO_2 , the deposition velocity in polluted regions of Europe has been increasing with time as the amounts of SO_2 have declined relative to ambient NH_3 concentration, allowing the surface resistance for SO_2 to decline substantially (Erisman et al., 1998, 2001; Fowler et al., 2001).

Potential non-linearities in source-receptor relationships were identified by Clark et al in the 1980s (Clark, Fisher, & Scriven, 1987). But at that time the magnitude of emission reductions was small relative to overall emissions and the available data series was short and geographically limited. The projected non-linearities were not therefore subjected to a significant test against long-term measurements of concentration and deposition fields. More recently, non-linearities in source receptor matrices computed with the EMEP model have been examined by Bartnicki (2000) who concluded that non-linearities were greatest for oxidized nitrogen and increased with distance between source and receptor and were also largest for pollutants with the smallest rates of deposition.

However, the study by Bartnicki was limited to numerical experiments and the available data in Europe now provides broad coverage at continental scales of the concentrations of the major ions in precipitation and hence wet deposition for in excess of 20 years (Tarrason et al., 2004). The monitoring also includes gaseous SO_2 and for much of the area NO_2 . Other important gases including HNO_3 and NH_3 are not monitored separately throughout Europe, and continuous monitoring of dry deposition is limited to a few locations in The Netherlands, Germany and the UK (Erisman et al., 1998).

Examination of the long term trends in emission and deposition in the UK has revealed substantial non-linearities in sulphur deposition, which are caused by a combination of increasing rates of SO_2 dry deposition and increasing imports of sulphur to the UK from shipping activities in the eastern Atlantic Ocean (Endresen et al., 2003).

The purpose of this paper is to examine the long term trends in emission and deposition at the regional scale in Europe using data from the EMEP model and measured gaseous and precipitation concentration fields throughout Europe in the period 1980–2000.

The background of the paper is the substantial reduction in emission of the primary pollutants SO_2 , NO_x and NH_3 between 1980 and the present, summarised in Fig. 1.

2 Materials and Methods

The analysis is in two parts, first an examination of the trends in emission and deposition for sulphur,

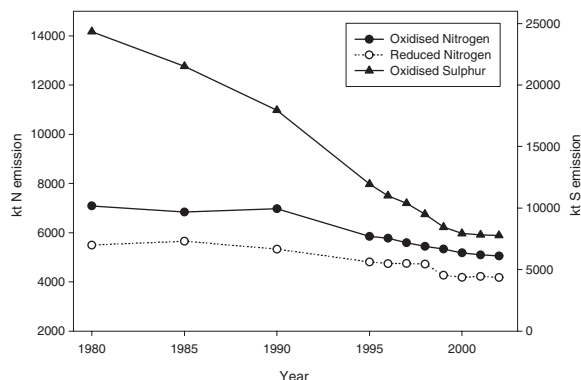


Fig. 1 Emissions of Sulphur, oxidised and reduced Nitrogen in the EMEP domain between 1980 and 2000

oxidized and reduced nitrogen from the EMEP model for the period 1980–2000 in five regions of Europe, roughly separated by their emission-deposition patterns into two source regions in which the emissions exceed the deposition and three receptor regions in which the deposition exceeds emissions within the zone by an incrementally larger fraction (Fig. 2).

The second part of the analysis is a comparison of emissions within the five zones with measured trends in concentrations of the relevant ions in precipitation, SO_4^{2-} , NO_3^- and NH_4^+ , and with ambient concentrations of SO_2 and NO_2 .

Measured Concentrations (annual Means) were allocated to the zones 1–5 shown in Fig. 3. Data were used only when data capture exceeded >75% of the sampling period. Annual mean values for each region for all years were calculated for sites with a

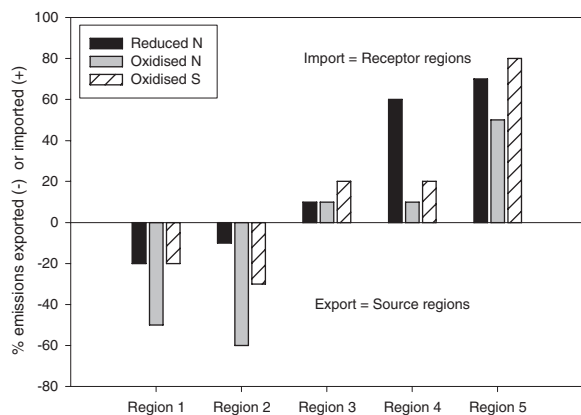


Fig. 2 Percentage of emissions exceeding deposition in source regions (% of emission exported) and percentage of deposition exceeding emission in receptor regions (% of emission imported)

data record of 10 years or more (allowing discontinuities). For trends (1980–2000), for both gaseous and liquid phase concentrations, the changes over the 20-year period were calculated from linear trend analysis as the average over the region.

Emission and deposition within each of the zones were calculated from the total deposition for whole domain allocated to each grid square to its region.

The overall mass balance over the entire EMEP domain (Fig. 4) shows emissions of sulphur approximately 10% smaller than deposition, indicating a net import to the domain, or a significant underestimate of emissions or overestimate of deposition, or a combination of the two. The marine emissions of sulphur were held constant in the model, yet recent studies of marine sulphur emissions shows a steady increase over the 20-year period (Derwent et al., 2005). Emissions and deposition of reduced nitrogen remain in close balance over the domain over the 20-year period. For oxidized nitrogen emissions exceed deposition throughout the period, indicating a net export from Europe to the east. However, the net export in 1980 equivalent to 10% of emissions has grown to 20% by 2000, and shows a substantial export of oxidized nitrogen to the east of the EMEP domain. The extent to which this apparent growth in exported nitrogen is the consequence of a growing contribution from shipping is not quantified in this analysis. It is possible that the entire growth is due to shipping sources, a priority area of further work.

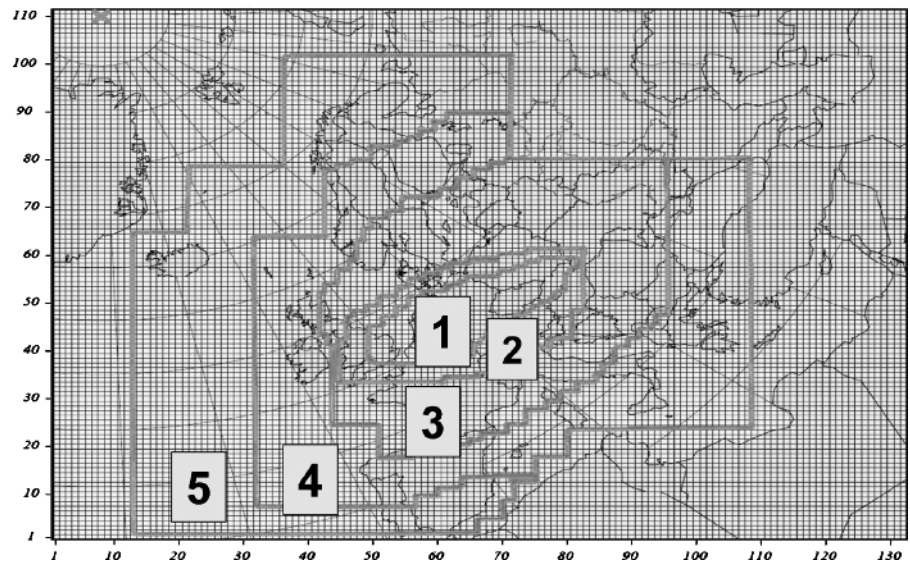
3 Comparisons Between Emissions and Deposition in the Source and Receptor Regions of Europe 1980–2000 Using EMEP Model Data

3.1 Source Regions

In these regions, comprising the highly populated region of northern Europe stretching from the Czech Republic in the East to SE England in the West, emissions exceed deposition for all pollutants considered, by between 10 and 60% (Table 1). Over the 20-year period emissions of sulphur decline by between 70 and 80% and deposition declines by a similar amount averaging 75% for the two regions (Table 2).

Similarly for oxidized and reduced nitrogen the reduction in emissions is close to the reduction in deposition at 20% for reduced nitrogen and 40% for

Fig. 3 EMEP grid divided into five regions



oxidized nitrogen. From the modelled data the changes in emission and deposition over the 20-year period are close to linear.

3.2 Receptor Regions

For Zone 3, a receptor region, deposition exceed emission by between 10 and 40% (1980), changing to 20% (2000) for oxidized nitrogen and sulphur, respectively, and the changes over the 20-year period show an approximately linear decline in emission and deposition (Table 3).

For the remote regions (Region 4) in which deposition within the region exceeds emissions by

between 40 and 80% in 1980 declining to 10–60% in 2000, there is a marked decline in advection into the region over the 20 years. However, these regions are still receiving substantially more deposition than the total of the emissions within the regions. The emissions declines for all three pollutants in the zone are smaller than the deposition declines, showing the effect of the greater reduction in the pollutant imported into the region. For zone 5 in which deposition exceeds emissions by between 80 and 150% for sulphur and reduced nitrogen, respectively, the deposition within the region is very sensitive to changes in sources upwind, and the decline in emissions within the region are smaller than the

Fig. 4 The mass budget for Sulphur and oxidised Nitrogen for 2000 showing a balance of emission and deposition, net import of sulphur into the domain and a net export of oxidised Nitrogen, figures in MTonnes S or N

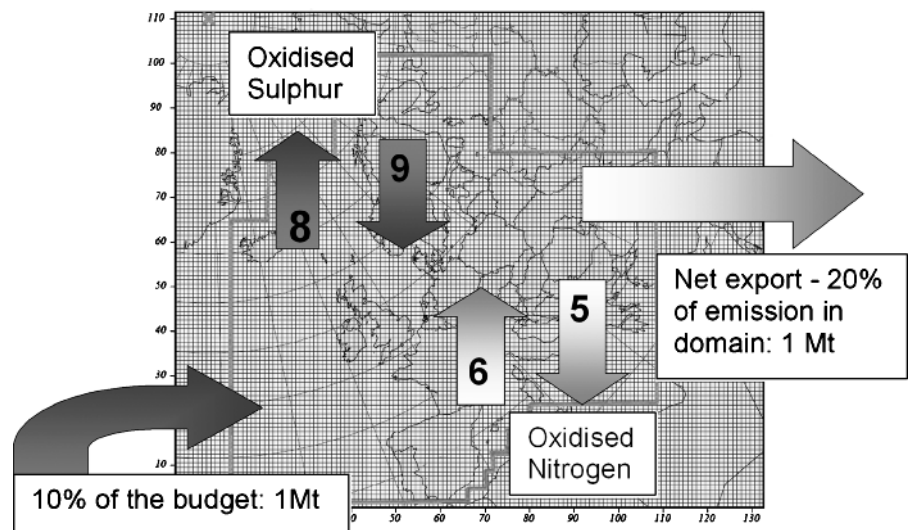


Table 1 Percentage by which emission exceeds pollutant deposition in zones 1 and 2 (zones from Fig. 3)

	Reduced Nitrogen(%)	Oxidised Nitrogen	Oxidised Sulphur
Region 1	20	50%	40% in 1980 20% in 2000
Region 2	10	40% in 1980 60% in 2000	30%

decline in deposition for both oxidized and reduced nitrogen.

4 Comparing Measured Concentrations in Air and Rain With Trends in Emissions

In this section, trends in emissions since 1980 are compared with trends in measured concentrations of SO_4^{2-} , NO_3^- and NH_4^+ in precipitation and gaseous NO_2 , and SO_2 from the EMEP network. In this case the trends are considered by pollutant.

4.1 Reduced Nitrogen

The emissions of ammonia declined by 23% over the 20 years over the entire domain, but there are different trends in the different zones (Fig. 5). Emissions decline by 20–30% in the source regions and much smaller reductions are observed in the receptor regions, of 6% in zone 4 and a small increase in emissions in zone 5 of 10%. The concentrations of NH_4^+ in rain decline in the source regions fairly closely in proportion to the emission reductions. In the receptor regions concentrations of NH_4^+ increase during the 20 years, although from very small values, consistent qualitatively with changes in emissions within the zone.

Table 2 Changes in emission and deposition from 1980–2000, expressed as percentage in regions 1 and 2 (in relation to 1980 value)

	Emission		Deposition	
	Region 1 in (%)	Region 2 in (%)	Region 1 in (%)	Region 2 in (%)
Reduced Nitrogen	–29	–22	–18	–18
Oxidised Nitrogen	–41	–31	–36	–34
Oxidised Sulphur	–83	–73	–77	–73

Table 3 Changes in emission and deposition from 1980–2000 in Region 3, expressed as percentage (in relation to 1980 value)

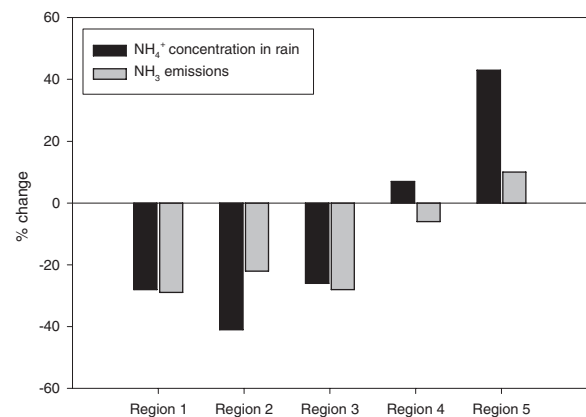
	Emission in (%)	Deposition in (%)
Reduced Nitrogen	–28	–23
Oxidised Nitrogen	–29	–30
Oxidised Sulphur	–61	–67

4.2 Oxidized Nitrogen

Emissions decline in the source regions by between 30 and 40% over the 20 years (Fig. 6). By contrast emissions in the remote regions decline by a smaller amount (2%) in zone 4 and increase by 6% in zone 5. The concentrations of NO_3^- in rain decline by much smaller amounts than the change in emissions, averaging –22% in the source regions. In the receptor regions the reductions in concentrations of NO_3^- in rain are smaller than reductions in emissions in zones 3 by almost a factor of three, and in the remote regions 4 and 5, concentrations increase by typically 50%. Ambient concentrations of NO_2 (Table 4) change in all regions except region 4 by amounts that are similar to the changes in emissions within the zone.

4.3 Sulphur

Emissions of sulphur decline in all zones, by 83% in zone 1 declining through the different zones to 52% in zone 5 over the 20 years. The concentrations of SO_2 also decline, and by amounts that consistently exceed the reductions in emissions (Fig. 7). The concen-

**Fig. 5** Changes in NH_4^+ in precipitation from 1980–2000, expressed as percentage of change relative to 1980

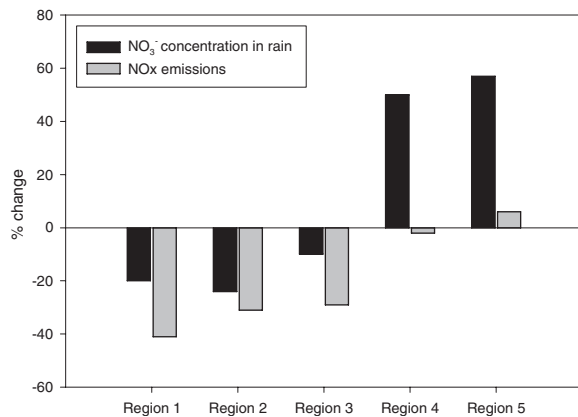


Fig. 6 Changes in NO_3^- in precipitation from 1980–2000, expressed as percentage of change relative to 1980

trations of SO_4^{2-} in rain also decline in all zones and in this case consistently by smaller amounts than the reduction in emissions, by amounts that exceed the reduction in emissions by 10–30% (Fig. 7).

5 Discussion

The comparison of emissions and deposition within the zones defined in this paper using the EMEP model data show a close correspondence of the values in the source areas for both oxidized and reduced nitrogen and for sulphur. In the remote regions the correspondence between emission and deposition is close for sulphur but some differences for oxidized and reduced nitrogen are apparent, showing the greater importance of long range transport to the deposition budgets of these regions. However, taken as a whole the picture generated by these data is one of an approximately linear system in which the trends in emission and deposition broadly follow the trends in deposition.

When the field measurements of concentrations of the pollutants in gas phase and in precipitation are considered, a rather different picture emerges. In the case of reduced nitrogen the measured concentrations

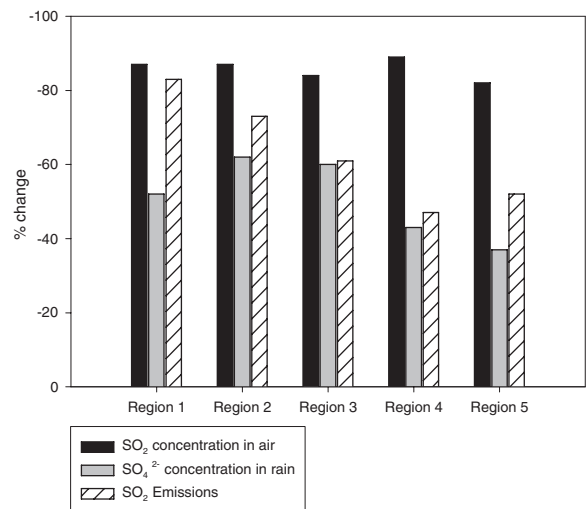


Fig. 7 Changes of SO_2 in air, non-sea salt SO_4^{2-} in precipitation and SO_2 emissions, expressed as percentage of change relative to 1980

of NH_4^+ and the emissions follow broadly similar trends over the majority of the domain, although there is a clear, increase in concentrations in the remote regions, even though the absolute values are small. For oxidized nitrogen there are clear non-linearities in the responses of deposition to the emission reductions over the 20 years. Concentrations of NO_2 follow the decline in emissions, but the reductions in NO_3^- concentrations in precipitation are much smaller than emission reductions, with some areas with reductions in emissions of 40% showing a reduction in concentrations in precipitation of 20%. In the remote regions emission reductions are much smaller, and in these regions the concentrations of NO_3^- are increasing. Over the two remote regions the concentrations, while small have increased by about 50% over the 20-year period and might be important for species adapted to a very limited atmospheric nitrogen supply. Thus for oxidized nitrogen there are large non-linearities, and these while indicated by the model data are much more pronounced in measurements than in the model. The observations of non-linearities in the oxidized nitrogen budget are consistent with observations at the country scale, with very much smaller reductions in the deposition of oxidized nitrogen in the UK than the reduction in emissions (Fowler, Muller, Smith, Cape, & Erisman, 2005).

The cause of these non-linearities remains a matter for speculation, but at the country scale, the data are consistent with more rapid oxidation of NO_x to NO_y ,

Table 4 Changes in NO_2 in air from 1990–2000, expressed as percentage of change relative to 1990

	Region 1 in(%)	Region 2 in (%)	Region 3 in (%)	Region 4 in (%)
ΔNO_2 in air	–37	–31	–21	–29
Δ Emission	–33	–30	–30	–9

through both homogeneous oxidation processes with OH as the oxidant, and the steady increase in mean ozone concentrations (Simmonds, Derwent, Manning, & Spain, 2004) is consistent with this explanation, at least qualitatively. The oxidation of NO_x to NO_y in the large urban conurbations at night represent another process subject to increases with time over the last decade as urban ozone concentrations have steadily increased.

For sulphur, the mass balance over the entire domain suggests the importance of additional sources outside the region, or that emissions have been underestimated. From the recent publications on increasing shipping sulphur emissions over the period 1980–2000, it seems probable that shipping emissions have been underestimated (Corbett & Koehler, 2003; Endresen et al., 2003). There are clear non-linearities, with ambient concentrations of SO₂ declining faster than emissions throughout the domain. The rapid decline in SO₂ concentration is entirely consistent with the observation of increasing deposition velocity for SO₂ with time as observed by Fowler et al. (2001). The underlying process causing this effect is the steady decline in the SO₂/NH₃ concentration ratio which allows the water film on vegetation to remain at a sufficiently high pH to maintain SO₂ uptake at the surface as shown in field data and a process based model by Flechard, Fowler, Sutton, & Cape, (1999).

The non-linearities in oxidized nitrogen and sulphur emission-deposition budgets are evident across substantial areas of the domain. The consequences for effects assessment can readily be quantified when the processes causing the non-linearities have been incorporated in the long-range transport models but are expected to be substantial. Current uncertainties in the processes leading to the non-linearities are therefore priorities for research and model development. The data sets available within Europe, from the networks and from campaign and laboratory measurements provide a key resource, but the main focus should be on the further, careful analysis of the field measurements and the development of the models to reproduce the observed trends.

Acknowledgements The Authors gratefully acknowledge the financial support of the European Commission through the NEPAP project and the UK Department for the Environment, Food and Rural Affairs (Defra) in contracts (EPG1/3/166).

References

- Bartnicki, J. (2000). Non-linear effects in the source-receptor matrices computed with the EMEP Eulerian acid deposition model. pp 34 EMEP/MSC-W Note 4/00.
- Clark, P. A., Fisher, B. E. A., & Scriven, R. A. (1987). The wet deposition of sulphate and its relationship to sulphur dioxide emissions. *Atmospheric Environment*, 21, 1125–1131.
- Corbett, J. J., & Koehler, H. W. (2003). Updated emissions from ocean shipping. *Journal of Geophysical Research*, 108, 4650, doi <http://dx.doi.org/10.1029/2003JD003751>.
- Brydges, T. G., & Wilson, R. B. (1991). Acid rain since 1985–times are changing. *Proceedings of the Royal Society of Edinburgh B*, 97, 1–16.
- Derwent, R. G., Stevenson, D. S., Doherty, R. M., Collins, W. J., Sanderson, M. G., Johnson, C. E., et al. (2005). The contribution from shipping emissions to air quality and acid deposition in Europe. *Ambio*, 34, 54–59.
- Endresen, O., Sorgard, E., Sundet, J. K., Dalsoren, S. B., Isaksen, I. S. A., Berglen, T. F., et al. (2003). Emission from sea transportation and environmental impact. *Journal of Geophysical Research*, 108, 4650, doi <http://dx.doi.org/10.1029/2002JD002898>.
- Erisman, J. W., Hensen, A., Fowler, D., Flechard, C. R., Gruner, A., Spindler, G., et al. (2001). Dry deposition monitoring in Europe. *Water, Air, and Soil Pollution, Focus* 1, 17–27.
- Erisman, J. M., Mennen, M. G., Fowler, D., Flechard, C. R., Spindler, G., Gruner, A., et al. (1998). Deposition monitoring in Europe. *Environmental Monitoring and Assessment*, 53, 279–295.
- Flechard, C. R., Fowler, D., Sutton, M. A., & Cape, J. N. (1999). A dynamic chemical model of bi-directional ammonia exchange between semi-natural vegetation and the atmosphere. *Quarterly Journal of the Royal Meteorological Society*, 125, 1–33.
- Fowler, D., Muller, J., Smith, R. I., Cape, J. N., & Erisman, J. W. (2005). Nonlinearities in source receptor relationships for sulphur and nitrogen compounds. *Ambio*, 34, 41–46.
- Fowler, D., Sutton, M. A., Flechard, C., Cape, J. N., Storeton-West, R., Coyle, M., et al. (2001). The control of SO₂ dry deposition on to natural surfaces by NH₃ and its effects on regional deposition. *Water, Air, and Soil Pollution, Focus* 1, 39–48.
- Grennfelt, P., & Hov, Ø. (2005). Regional air pollution at a turning point. *Ambio*, 34, 2–10.
- Johnson, D. W., & Reuss, J. O. (1984). Soil-mediated effects of atmospherically deposited sulphur and nitrogen. *Philosophical Transactions of the Royal Society of London. B*, 305, 383–392.
- Simmonds, P., Derwent, R. G., Manning, A. L., & Spain, G. (2004). Significant growth in surface ozone at mace head, Ireland, 1987–2003. *Atmospheric Environment*, 38, 4769–4778.
- Tarrason, L., Fagerli, H., Jonson, J. E., Klein, H., van Loon, M., Simpson, D., et al. (2004). Transboundary acidification, eutrophication and ground level ozone in Europe. EMEP Status Report 1/04, pp. 154.
- Wayne, R. P. (1985). *Chemistry of atmospheres*. New York: Oxford University Press. (pp. 361)

Trends in Chemical Composition of Wet-only Precipitation at Rural French Monitoring Stations Over the 1990–2003 Period

Pierre Sicard · Patrice Coddeville ·
Stéphane Sauvage · Jean-Claude Galloo

Received: 17 June 2005 / Revised: 17 January 2006 / Accepted: 12 February 2006 / Published online: 3 March 2007
© Springer Science + Business Media B.V. 2007

Abstract The long-term monitoring of precipitation and its chemical composition are important for identifying trends in rain quality and for assessing the effectiveness of pollution control strategies. A statistical test has been used to the atmospheric concentrations measured in the French rural monitoring network (MERA) in order to bring out spatio-temporal trends in precipitation quality in France over the period 1990–2003. The non-parametric Mann–Kendall test which has been developed for detecting and estimating monotonic trends in the time series was used and applied in our study at annual values of wet-only precipitation concentrations. The emission data suggest that SO_2 and NO_x emissions decreased (-3.3 and -2.0% year $^{-1}$, respectively) contrary to NH_3 emissions that increased slightly ($+0.2\%$ year $^{-1}$) over the period 1990–2002 in France. On the national scale, the pH values have a significant decreasing trend of -0.025 ± 0.02 unit pH year $^{-1}$. SO_4^{2-} and $\text{nss} - \text{SO}_4^{2-}$ concentrations in precipitation have a significant decreasing trend, -3.0 ± 1.6 and $-3.3 \pm 0.6\%$ year $^{-1}$, respectively, corresponding with the downward trends in SO_2 emissions in France (-3.3% year $^{-1}$). A good correlation ($R^2=0.84$) between SO_2 emissions and

$\text{nss} - \text{SO}_4^{2-}$ concentrations was obtained. The decreasing trend of NH_4^+ was more significant ($-5.4 \pm 5.2\%$ year $^{-1}$) than that of NO_3^- ($-1.3 \pm 2.4\%$ year $^{-1}$). Globally, the concentration of the major ions showed a clear downward trend including marine and alkaline ions. In addition, the relative contribution of HNO_3 to acidity precipitation increased by 51% over the studied period.

Keywords Acid rain · Mann–Kendall test · Sen's method · Spatial trend · Temporal trend · Trends analysis

1 Introduction

During the last 25 years, much attention has been devoted to acid rain. The main reason for acidification is the emissions of sulphur and nitrogen compounds (SO_2 , NO_x and NH_3) into the atmosphere. A part of these compounds participates in the acid rain phenomenon and contributes to water acidification, soil depletion, plants and animals disappearance, forest damage, cultural heritage erosion and other problems. In fact, the pollutants that cause acidification also play a part in other environmental problems like eutrophication, ground level ozone and climate change.

Emissions of sulphur are the primary source of acidification. The major source of SO_2 is the combustion of sulfur-containing fuels (Harrison 1987). Nitric oxide is produced from the reaction of N_2 and O_2 in air during high temperature combustion

P. Sicard · P. Coddeville (✉) · S. Sauvage · J.-C. Galloo
Ecole des Mines de Douai, Département Chimie et
Environnement, 941 rue Charles Bourseul BP 838,
59508 Douai, France
e-mail: coddeville@ensm-douai.fr

processes as well as from oxidation of nitrogen in the fuel. More than half of the emissions in Europe come from road traffic and most of the rest from combustion plants. Then, gaseous SO_2 is converted to sulphuric acid aerosols and sulphates and gaseous NO_x to nitric acid and nitrates in the atmosphere (Harrison 1987). Ammonia (livestock farming) is another nitrogen compound that contributes to the acidification of soil and water (Weijers and Vugts 1990).

Oxides of sulphur and nitrogen can be transported on long distances by air masses. This means that the problem of acidification knows no borders and it's the reason why many countries have created a monitoring network. Most networks in Europe were implemented at the beginning of 80s under the Convention for the Long Range Transport of Air Pollutants (CLRTAP, 1979). An important objective of many environmental monitoring programs is to detect changes or trends in pollution levels over time.

Many studies on temporal trends in chemical composition of precipitation have been conducted in Europe (Avila 1996; Hayman 2004; Hünová et al. 2004; Puxbaum et al. 1998), North America (Kelly et al. 2002; Lehmann et al. 2005; Lynch et al. 1995; Nilles and Conley 2001), Japan and India (Fujita et al. 2000; Seto et al. 2002). According to these previous studies, it is necessary to evaluate the long term trends in chemical composition of precipitation in order to understand and assess the impact on concentration from the changes of air pollutant emissions.

This paper describes the spatial and temporal trends observed in concentrations of main precipitation components collected in the 11 sites of the French rural monitoring network over the period 1990–2003.

2 Sampling Sites and Chemical Analysis

In 1984, a French rural monitoring network, including five stations, was implemented by the French Ministry of Environment and the Environmental Agency ADEME. In January 1990, this network was extended at 11 stations and called MERA (Plaisance et al. 1996). The objectives were to create a long term high quality data base for the development of geographic patterns and temporal trends in atmospheric deposition. In 2004, nine stations integrated the European network EMEP (European Monitoring and Evaluation Program). Figure 1 shows the geographic location of these

stations and Table 1 shows the characteristics of each station in 2003. All sites were located in rural areas, widely distributed over the French territory and were generally not influenced by local anthropogenic emission sources.

All stations are equipped with the same automatic wet-only collector opened only during rain or snow period. A quality assurance program was set up from 1995, according to the recommendations of EMEP program, it concerns the routine handling, shipping, laboratory analyses and data acquisition. The samples were analyzed for anions (Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} and NH_4^+) by ion chromatography with a conductimetric detection. The mean concentrations are calculated as volume weighted averages.

The aim of the present study is perform trend analysis of wet precipitation data collections from 11 sampling sites all over France for the period 1990–2003. Additionally, the trend analysis results will be compared and interpreted with respect to data from the total emissions of pollutants (SO_2 , NO_x and NH_3).

3 Detection and Estimation of Trends

The detection and estimation of trends are complicated by problems associated with the characteristics of

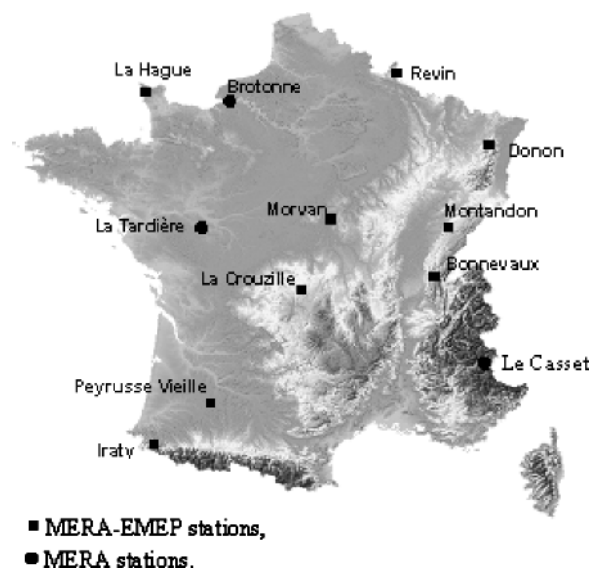


Fig. 1 Geographic locations of the French rural atmospheric deposition monitoring network (MERA) stations in 2003

Table 1 Characteristics of French rural monitoring stations

Station	L at -Long	Altitude (m)	Environment	Period
Brotonne	49N–0W	115	Forest	1990–2003
Bonnevaux	465N–6E	836	Plain	1990–1998
Donon	48N–7E	775	Forest	1990–2003
Iraty	43N–1W	1,300	Mountain	1990–2003
La Crouzille	45N–1E	497	Plain	1990–2003
La Hague	49N–1W	133	Coastal	1990–2003
La Tardiere	47N–0.7W	143	Valley	2001–2003
Le Casset	45N–6E	1,750	Mountain	1990–2003
Montandon	47N–6E	836	Plain	1998–2003
Morvan	47N–4E	620	Plain	1990–2003
P. Vieille	43N–2E	200	Valley	1995–2003
Revin	50N–4E	390	Forest	1990–2003

pollution data. During the past decades, numerous parametric and non-parametric techniques for the detection of long-term trends in time series have been developed (Hirsch et al. 1991; Sirois 1998). The main objective of the trend analysis is to know if there is a significant change in the time series. The advantage of the non-parametric statistical tests over the parametric tests is that the non-parametric tests are more suitable for non-normally distributed, missing data and extreme values, which are frequently encountered in environmental time series (Yue and Pilon 2002). These tests can be applied to small number of observations. However, it is in general necessary to have independent observations.

The non-parametric techniques presented in this section are applicable when the time series can be written in the following form (1):

$$X_i = f(t_i) + \epsilon_i \quad (1)$$

with X_i the observation of the compound i and $f(t_i)$ a continuous monotonic increasing or decreasing function of time. The residuals ϵ_i are assumed to belong to the same distribution with zero mean. The variance of the distribution is stationary. The data can be annual, monthly, weekly data for a given site.

3.1 The Mann–Kendall Test

The Mann–Kendall test is a non-parametric statistical test to detect the presence of a monotonic increasing or decreasing trend within a time series in absence of any seasonal variation or other cycles. Many data in

atmospheric chemistry have a seasonal variation, then, the Mann–Kendall test is limited to annual data to be free from the problem of seasonal variation and autocorrelation.

The bibliography using the Mann Kendall test, recommended by the WMO, is abundant and universal: hydrology (Yue and Pilon 2002), climatology, air quality (De Leeuw 2000; Holland et al. 2004) and precipitation chemistry (Kvaalen et al. 2002; Nilles and Conley 2001). There is a sequence of observations $X_1, X_2, \dots, X_n$ and we want to test the following hypothesis: H_0 , the observations X_i are randomly ordered, no trend, against the alternative hypothesis, H_1 where there is an increasing or decreasing monotonic. For time series with less than 10 values, the S test is used (Gilbert 1987) while normal approximation Z is used when we have 10 values or more. The number of annual values in this study is denoted by n and the missing values are allowed.

3.1.1 Number of Values < 10

The statistical S test is defined as following (2):

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(x_j - x_k) \quad (2)$$

$$\text{with } \text{sgn}(x_j - x_k) = \begin{cases} 1 & \text{si } x_j - x_k > 0 \\ 0 & \text{si } x_j - x_k = 0 \\ -1 & \text{si } x_j - x_k < 0 \end{cases}$$

where x_j and x_k are the annual values for the year j and k ($j > k$) and expectation values $E(S) = 0$. If $S > 0$,

we noted an increasing monotonic trend and if $S < 0$, the trend is decreasing and monotonous.

3.1.2 Number of Values ≥ 10

If n is higher than 10, we use the normal approximation Z test. Moreover, if there are several equal values in the time series, the quality of this approximation may be reduced. The S variance can be written in the following form (3):

$$\text{Var}(S) = \frac{n(n-1)(2n+5) - \sum_{p=1}^q tp(t_p-1)(2t_p+5)}{18} \quad (3)$$

Here q is the number of tied groups and t_p is the number of data values in the p th group. The value of S and $\text{Var}(S)$ are used to determine the Z test statistic and is written in the following form (4):

$$Z = \begin{cases} \frac{S-1}{\sqrt{\text{Var}(S)}} & \text{if } S > 0 \\ 0 & \text{if } S = 0 \\ \frac{S+1}{\sqrt{\text{Var}(S)}} & \text{if } S < 0 \end{cases} \quad (4)$$

The presence of a statistically significant trend is evaluated using the Z value. If $Z > 0$ then we note an increasing monotonic trend and if $Z < 0$, the trend is decreasing and monotonous.

The “critical area” of the statistical Mann–Kendall test is given by $S < Z_{\alpha/2} \sqrt{\text{Var}(S)}$ or $S > Z_{1-\alpha/2} \sqrt{\text{Var}(S)}$ where $Z_{\alpha/2}$ et $Z_{1-\alpha/2}$ are respectively, the $\alpha/2$ and $1-\alpha/2$ quantiles of the normal distribution and $\text{Var}(S)$ the variance of the statistical S test. The H_0 hypothesis is accepted if $|Z| \leq Z_{\alpha/2}$ and $F_N(Z_{\alpha/2}) = \alpha/2$, F_N is related to cumulative standard normal distribution. The α level is the probability of rejecting the null hypothesis H_0 when it is true. The smaller the value of α , the more confidence there is that the null hypothesis is really false when it has been identified as such. The test is used for four different significance levels α : 0.1, 0.05, 0.01 and 0.001.

3.2 Sen’s Estimator Slope

For estimating the trend, a consistent nonparametric estimator for the coefficients of a linear regression was proposed and modified by Sen (1968) to include

the possibility of ties in the t_i . We consider that $f(t_i)$ in the relation (1) is equal to $f(t) = Qt + B$ where Q is the slope and B is a constant. The first estimator assumes that no seasonal cycle is present in data. This non-parametric method is used if the trend can be considered linear. If there are n values for the pair (t_i, X_i) , the coefficient of the linear relation is defined as the n values of $A_{ij} = \frac{(x_i - x_j)}{(t_i - t_j)}$ for $i = 1, 2, \dots, n$ ($j = 1, 2, \dots, n; j > i, t_i \neq t_j$). The Sen coefficient estimation Q is the median of these n values A_{ij} (after ordering the A_{ij}) and Sen’s estimator is:

$$Q = \begin{cases} A(n+1)/2 & \text{if } n \text{ is odd} \\ \frac{1}{2}(A(n/2) + A(n+2)/2) & \text{if } n \text{ is even} \end{cases} \quad (5)$$

The $(100(1-\varepsilon)\%)$ confidence interval about the slope estimate is obtained by the non-parametric technique based on a normal distribution.

In general, we calculate the confidence interval with two levels $\varepsilon = 0.01$ (99%) and $\varepsilon = 0.05$ (95%) and resulting in two different confidence intervals. To estimate B , we calculate n values $X_i - Qt_i$ and the median value gives an estimate of B (Sirois 1998). The Sen method is little affected by errors within the data values and it is robust because insensitive to the “extreme” and missing values.

4 Results and Discussion

In coastal regions a substantial fraction of the measured SO_4^{2-} is due to the presence of the sea-salt. Thus, in order to estimate the SO_4^{2-} , Ca^{2+} , Mg^{2+} , Cl^- and K^+ from the other sources (mostly acidic), it is common practice to use a “tracer” with a known ratio to SO_4^{2-} in bulk sea-water and subtract the appropriate amount of the tracer in the precipitation. Na^+ , Cl^- or Mg^{2+} can be used as tracers, but Na^+ is preferred since there are other potential sources of Cl^- (industrial processes) and Mg^{2+} (wind-blown dust) in the atmosphere.

The average concentrations for the 11 sites are presented in the Table 2. The results of annual average changes and standard deviations calculated with the Mann Kendall test are presented in the Table 3.

Table 2 Average concentrations and standard deviations of precipitation constituents from 11 stations of the MERA network (mg l^{-1}) in France over the period 1990–2003

Stations	Period	Ionic concentrations (mg/l)													
		pH	Cl ⁻	b _{nss} -Cl ⁻	S-SO ₄ ²⁻	nss-SO ₄ ²⁻	N-NO ₃ ⁻	Na ⁺	Mg ²⁺	nss-Mg ²⁺	Ca ²⁺	Nss-Ca ²⁺	K ⁺	Nss-K ⁺	N-NH ₄ ⁺
Donon	1990–2003	4.89±0.1	0.41±0.1		0.42±0.1		0.31±0.1	0.23±0.1	0.05±0.01		0.18±0		0.06±0.02		0.49±0.2
Revin	1990–2003	4.91±0.1	0.75±0.1		0.45±0.1		0.33±0.2	0.44±0.1	0.07±0.02		0.22±0		0.05±0.01		0.46±0.1
Morvan	1990–2003	5.14±0.2	0.57±0.1	0.19±0.1	0.38±0.1	0.36±0.1	0.26±0.1	0.32±0.1	0.08±0.01	0.04±0.03	0.30±0.1	0.29±0.1	0.08±0.05	0.08±0.04	0.53±0.3
Montandon	1998–2003	5.01±0.1	0.26±0.1		0.32±0.1		0.30±0.1	0.15±0	0.03±0		0.29±0.1		0.04±0.01		0.34±0.1
Bonnevaux	1990–2003	5.15±0.2	0.37±0.1		0.35±0.1		0.23±0.1	0.21±0.1	0.07±0.02		0.34±0.1		0.04±0.02		0.49±0.2
La Hague	1990–2003	4.99±0.2	13.07±12	4.57±4.6	1.04±0.8	0.60±0.4	0.35±0.1	7.27±6.5	1.00±1.00	0.18±0.3	0.53±0.3	0.38±0.2	0.41±0.50	0.27±0.40	0.57±0.4
Brottonne	1990–2003	4.94±0.2	2.18±0.9	0.76±0.4	0.59±0.1	0.51±0.1	0.29±0.2	1.21±0.5	0.19±0.10	0.05±0.02	0.26±0.1	0.24±0.1	0.08±0.03	0.06±0.02	0.63±0.3
Italy	1990–2003	5.12±0.1	0.73±0.2	0.21±0.1	0.51±0.1	0.48±0.2	0.28±0.1	0.44±0.1	0.11±0.10	0.06±0.06	0.58±0.2	0.57±0.2	0.09±0.10	0.08±0.10	0.53±0.3
P. Vieille	1995–2003	5.00±0.2	1.50±0.5	0.47±0.2	0.51±0.1	0.46±0.1	0.28±0.1	0.88±0.3	0.13±0.10	0.03±0.01	0.43±0.1	0.42±0.1	0.09±0.02	0.08±0.03	0.37±0.1
La	1990–2003	5.22±0.1	1.33±0.2	1.06±0.1	0.44±0.1	0.40±0.1	0.25±0.1	0.65±0.2	0.13±0.11	0.06±0.02	0.33±0.1	0.32±0.1	0.07±0.03	0.06±0.02	0.54±0.2
Crouzille															
Le Casset	1990–2003	5.30±0.2	0.18±0.1		0.33±0.1		0.20±0.1	0.10±0.1	0.05±0.01		0.80±0.5		0.10±0.10		0.31±0.2
Mean	1990–2003	5.07±0.1	2.06±1.4	0.87±1.3	0.50±0.1	0.43±0.1	0.29±0.1	1.15±0.7	0.19±0.1	0.06±0.03	0.40±0.1	0.37±0.1	0.11±0.1	0.08±0.04	0.50±0.2
Median	1990–2003	5.08±0.1	1.80±1.3	0.60±0.5	0.48±0.1	0.44±0.1	0.28±0.1	1.05±0.8	0.16±0.1	0.05±0.04	0.37±0.1	0.36±0.1	0.10±0.05	0.08±0.03	0.43±0.2

^a nb events rainy events numbers.^b nss sea-salted corrected.

Table 3 Annual average changes and standard deviations of precipitation constituents from 11 stations of the MERA network (% year⁻¹ and unit pH year⁻¹) obtained by the Mann–Kendall test in France over the period 1990–2003

Stations	Period	Annual average changes (% year ⁻¹ and unit pH year ⁻¹)											
		pH	Cl ⁻	S-SO ₄ ²⁻	a _{nss} -SO ₄ ²⁻	N-NO ₃ ⁻	Na ⁺	Mg ²⁺	nss-Mg ²⁺	Ca ²⁺	nss-Ca ²⁺	K ⁺	N-NH ₄ ⁺
Donon	1990-2003	-0.01**	-1.8*	-3.6****		-1.3*	-1.1	-5.0**		-1.8***		-5.6**	-4.6****
Revin	1990-2003	b _{ns}	-2.8**	-3.4****		-1.5***	ns	-2.2*		ns		+3.3	-5.1****
Morvan	1990-2003	-0.03***	-1.3**	-3.1****	-3.1****	ns	ns	-5.0***	-7.3****	-2.2	-2.2	+10.0**	-5.4****
Montandon	1998-2003	+0.03	0	+2.4	+8.7*		0	-7.5		-2.0		0	ns
Bonnevaux	1990-2003	-0.01	+7.8	-4.3****		ns	+11.7**	+1.7		-3.4		0	-7.5****
La Hague	1990-2003	-0.05*****	-2.2**	-3.1****	-2.7****	-2.7****	-2.2***	-2.2***	-2.5	-3.9*****	-3.3***	-3.8***	-1.9****
Brotonne	1990-2003	-0.04*****	-4.2****	-2.9****	-2.7****	0	-2.4**	-4.0***	-5.6***	-1.1	-5.6***	0	-5.7****
Iraty	1990-2003	-0.02**	+3.6	-3.5****	-3.7*	-1.6*	+4.1**	-2.3**	-6.0***	ns	-6.0***	+2.5	-5.4****
P. Vieille	1995-2003	-0.02*	-3.7	-1.7	ns	+1.9*	-2.8	-4.3	-5.3**	ns	-5.3**	-2.2	-3.8*
La Crouzille	1990-2003	-0.03***	ns	-2.8****	-2.2	-1.5**	ns	ns	-1.4	ns	-1.4	+3.8**	-6.0****
Le Casset	1990-2003	+0.01	+6.15	-2.2*	0	0	+3.8	+5.0		+10.7**		+1.4	-6.4****
Mean	1990-2003	-0.025 ⁺⁺⁺ ±0.02	-3.3 ⁺⁺ ±3.5	-3.0 ⁺⁺⁺ ±1.6	-3.3 ⁺⁺ ±0.6	-1.3 ⁺ ±2.4	-3.1 ⁺ ±4.3	-39 ⁺ ±2.7	-4.6 ⁺⁺⁺ ±2.2	-15±3.1	-19±2.7	-33 ⁺⁺⁺ ±4.1	-5.4 ⁺⁺⁺ ±5.2

^a *nss* sea-salted corrected

^b *ns* non significant

^c significance levels: $\alpha=0.001$ ****, 0.01***, 0.05**, 0.1*, >0.1.

4.1 Annual Trends of National Emissions

The Mann–Kendall test has been used for the French emissions of SO_2 , NO_x and NH_3 . Over the period 1990–2002, we obtained a decreasing trend of $3.3\% \text{ year}^{-1}$ ($\alpha=0.001$) for SO_2 . This decreasing trend began at the beginning of the 1980s. The main reasons are: nuclear development, use of charged sulfur fuels, catalytic exhaust pipes in transport... The NO_x emissions show a decreasing trend less important with an annual change rate of $-2.0\% \text{ year}^{-1}$ ($\alpha=0.001$) over the same period. The NO_x emissions remain dominated by the road transport (49%) although its contribution has been in regular reduction since 1993, translating the progressive consequences of the vehicles equipment into catalytic exhaust pipes. The NO_x emissions are going on decreasing in particular because of the improvements induced by the program “auto-oil.” These decreasing trends are compatible with the rather constraining objectives planned for 2010 by the Gothenburg protocol which imposes a reduction of 19% for the SO_2 emissions and of 30% for the NO_x emissions compared to the current levels. Contrary, NH_3 emissions increased slightly ($+0.2\% \text{ year}^{-1}$, $\alpha=0.1$). The objective is reached but in absence of measurements, the possible increasing in livestock could make more difficult the constraining objectives planned for 2010.

4.2 Annual Trends for pH Values

The most acidic pH values (annual $\text{pH}<5.0$) are found in the north-east of France, an area exposed to the eastern continental flux often charged in sulfur compounds (Charron et al. 2000). The urban and industrial activities located in the North (United Kingdom, Benelux and Germany) are also at the origin of this acidity. The pH values for the sites under marine influences are about 5.0. For the high-lying stations and the agricultural areas a higher value pH is observed. Calcium from the basic species CaCO_3 , dust particles and the ammonia neutralize the acidity of precipitation (Loye-Pilot et al. 1986). We can observe a small gradient (East–West) of the pH values distribution in France and no significant spatial distribution of the annual change rates. On the national scale, the average pH of precipitation over the period 1990–2003 (Table 2) is of 5.07 ± 0.1 with an annual average change (Table 3) of -0.025 ± 0.02

unit pH year^{-1} ($\alpha=0.001$). The main observation concerns the pH values which decrease while the emissions of acidifying components decrease. That could be related to decrease in base cation and NH_4^+ concentrations. The similar trends in pH value have occurred ($-0.022 \text{ unit year}^{-1}$) in France by Marín et al. (2001) whereas an increasing trend has occurred in Austria (Puxbaum et al. 1998), in Germany (Zimmermann et al. 2003) and at European scale (Vesely et al. 2002).

4.3 Annual Trends for SO_4^{2-}

SO_4^{2-} is the clearly identified compound as tracer of industrial pollution, but a part has its origin from enrichment by marine spray. The highest concentrations are found in northern France (Donon, Revin and Brotonne), areas “downwind” of large industrial complexes, then, under the direct influence of the air masses coming from the SO_2 emitters countries: England, Benelux and the North Sea (Charron et al. 1998, 2000). The lowest concentrations over the period 1990–2003 are observed in the high-lying stations: very little influenced and distant from polluted air masses. In addition, the concentrations in SO_4^{2-} decrease with the altitude. However, no significant spatial distribution of the annual change rates is identified. On the national scale, the average SO_4^{2-} concentration (Table 2) in precipitation over the period 1990–2003 is $0.50\pm0.1 \text{ mgS.l}^{-1}$ with a decreasing significant trend (Table 3) of $3.0\pm1.6\% \text{ year}^{-1}$ ($\alpha=0.001$) and of $0.43\pm0.1 \text{ mgS.l}^{-1}$ with a decreasing significant trend of $3.3\pm1.6\% \text{ year}^{-1}$ ($\alpha=0.01$) for nss-SO_4^{2-} . This decreasing is linked to the reduction policy of the SO_2 emissions established more than for 20 years ($-3.3\% \text{ year}^{-1}$).

By linear regression, a good empirical correlation between SO_2 emissions and average SO_4^{2-} precipitation concentration ($R^2=0.70$) and SO_2 emissions and average nss-SO_4^{2-} precipitation concentration ($R^2=0.83$) was calculated over the 1990–2003 period. The relationship between anthropogenic emissions of SO_2 and the SO_4^{2-} concentrations in precipitation may be significantly different from proportionality. This could be due to complex nonlinear chemical and physical transformation processes occurring in the atmosphere, or to the existence of large natural emissions. For example, changes in the concentrations of the $\text{OH}^\bullet$ radical caused by changes in the emissions of oxides

of nitrogen may influence the rate of transformation of SO_2 to SO_4^{2-} (Leck and Rodhe 1989). The similar trends in concentration of SO_4^{2-} in precipitation have occurred in Europe and North American due to the abatement strategies for SO_2 emissions since the 1960s (Avila 1996; Puxbaum et al. 1998).

4.4 Annual Trends for NO_3^-

Over the period 1990–2003, the highest NO_3^- concentrations were found in the stations of the northern and the north-eastern of France. The NO_x are emitted mainly by “road transport” sources. There is a strong density of population in these areas which are under the direct influence of the NO_x transmitting countries (Benelux, Germany and England) (Charron et al. 1998, 2000). The lowest concentration is observed in the altitude station (Le Casset): this station is very slightly influenced by air masses coming from emitting areas. These concentrations reflect the NO_x background concentrations trends in the ambient air. The concentrations are high in the areas “downwind” of large industrial complexes and with a strong density of population. The concentrations distribution appears homogeneous in the Center and South-west of France. No significant spatial distribution of the annual average change appears. In France, the average NO_3^- concentration (Table 2) over the period 1990–2003 is $0.29 \pm 0.1 \text{ mgN.l}^{-1}$ with a significant decreasing trend (Table 3) of $1.3 \pm 2.4\% \text{ year}^{-1}$ ($\alpha=0.05$). This reduction reflects the NO_x emissions reduction over that period ($-2.0\% \text{ year}^{-1}$).

The $[\text{NO}_3^-]/[\text{nss}-\text{SO}_4^{2-}]$ ratio in precipitation is useful in evaluating the relative contribution of H_2SO_4 and HNO_3 to the acidity of precipitation (Galloway et al. 1982). In the large area, this ratio showed clearly increasing trends and indicated that the relative importance of HNO_3 in the precipitation increased by 51% on average ($\alpha=0.001$) from 0.503 in 1990 to 0.839 in 2003 with an increasing significant trend of $4.0\% \text{ year}^{-1}$ ($\alpha=0.001$).

The temporal variation of the $\text{NO}_3^-/\text{nss}-\text{SO}_4^{2-}$ ratio in the precipitation is similar to those of the NO_x/SO_2 emission ratio. The increasing contribution of HNO_3 to acidification has been also reported in Spain, Japan and South Korea (Avila 1996; Fujita et al. 2000).

4.5 Annual Trends for NH_4^+

NH_4^+ dominates the precipitation chemistry of the West and the Center of France due to its intense agricultural activity. Ammonium is the indicator of intensive breeding and the ammonium nitrate fertilization cause the gas ammonia emanation. The highest concentrations are found in the North of France because of the Benelux countries influences. The lowest concentration over the period 1990–2002 is observed in the altitude station: Le Casset which is a non agricultural zone. If we consider the studied period (1990–2003) the concentration and the annual change rates distributions are homogeneous within the French territory. The average NH_4^+ concentration (Table 2) in precipitation over France is $0.50 \pm 0.2 \text{ mgN.l}^{-1}$ with a significant decreasing trend (Table 3) of $5.4 \pm 5.2\% \text{ year}^{-1}$ ($\alpha=0.001$). Even if the NH_4^+ measurements were not optimized in the past because the samples were not cooled during the sampling and handling, this trend is significant.

4.6 Annual Trends for Ca^{2+} , Mg^{2+} and K^+

The highest concentrations (Table 2) are found in the stations of the South of France, exposed clearly to the calcic contributions of Saharan origin and are minimal in the North-eastern quarter. The highest calcium concentrations correspond to the low acidity zones (neutralizing agent). The impact of this dust on the pH of precipitation was already observed in France by many authors (Loye-Pilot et al. 1986). The Ca^{2+} ion has a great contribution in the processes of neutralization of the acidity of precipitation (Munger 1982).

The lowest K^+ concentrations are found in the North-eastern quarter of France. Maximum K^+ concentrations are located in the West of the territory, under oceanic influence (marine spray) and the minima are located in the East region. This spatial distribution is similar with those of calcium. For all components, annual change rates (Table 3) do not present particular and significant spatial distribution. Over the period 1990–2003, the average Ca^{2+} concentration presents a decreasing trend of $1.5 \pm 3.1\% \text{ year}^{-1}$ ($\alpha>0.1$) and of $1.9 \pm 2.7\% \text{ year}^{-1}$ ($\alpha>0.1$) for $\text{nss}-\text{Ca}^{2+}$. The cause of the decline is most likely a consequence of reduced emissions of non-marine Ca^{2+} from combustion plant. *Le Casset* station are increasingly influenced by Saharan origin fluxes

(+10.7% year⁻¹, $\alpha=0.05$) as showed by Charron et al. (2000). The average Mg²⁺ and K⁺ concentrations present a decreasing trend of $3.9\pm2.7\%$ year⁻¹ ($\alpha=0.01$) and $3.3\pm4.1\%$ year⁻¹ ($\alpha=0.01$), respectively.

4.7 Annual Trends for Na⁺ and Cl⁻

These two elements are the major elements of precipitation in France and indicators of the marine influence. The highest Na⁺ and Cl⁻ concentrations (Table 2) are obtained in the North-Western quarter, the nearest of the sea. Minimum concentrations are found in the East of France. The highest annual change rates (Table 3) are obtained for the coastal stations. The altitude stations show an increasing trend in Na⁺ and Cl⁻. The Na⁺ and Cl⁻ distributions and trends are similar to those observed for the Mg²⁺. These three ions have the same origin and are characteristics of the air masses coming from the west. On the national scale, the average Na⁺ concentration in precipitation over the period 1990–2003 was 1.15 ± 0.7 mg l⁻¹ with a decreasing trend of $3.1\pm4.3\%$ year⁻¹ ($\alpha=0.05$). The average Cl⁻ and nss-Cl⁻ concentrations in precipitation over the same period are 2.06 ± 1.4 mg l⁻¹ and 0.87 ± 1.3 mg l⁻¹ respectively with a decreasing trend of $3.3\pm2.5\%$ year⁻¹ ($\alpha=0.01$) for Cl⁻ and of $4.2\pm2.1\%$ year⁻¹ ($\alpha=0.01$) for nss-Cl⁻.

This could be related to reductions in anthropogenic Cl emissions (incineration, HCl gas produced by papers industries and volcanic eruptions...). Moreover, these trends are coupled to observed climatic conditions.

5 Conclusion

After a long period of French atmospheric deposition program, it appeared necessary to study the long-term trends in chemical composition of precipitation in order to understand and assess the impact on chemical composition of precipitation from the changes of air pollutant emissions. On the national scale, the pH values have a significant decreasing trend of -0.025 ± 0.02 unit pH year⁻¹. The pH values decrease when emissions of acidifying components decrease. This could be related to decreases in base cation and NH₄⁺ concentrations. SO₄²⁻ and nss-SO₄²⁻ in precipitation have a significant decreasing trend, -3.0 ± 1.6 and $-3.3\pm0.6\%$ year⁻¹, respectively, corresponding with

the downward trends in SO₂ emissions in France (-3.3% year⁻¹). The decreasing trend of NH₄⁺ was more significant ($-5.4\pm5.2\%$ year⁻¹) than that of NO₃⁻ ($-1.3\pm2.4\%$ year⁻¹). The analytical method change for NH₄⁺ can explain the strong annual average change.

Globally, the concentration of the major ions showed a clear downward trend including marine and alkaline ions and those main reductions have reflected the reduction policy of the SO₂ and NO_x emissions over twenty years. The data suggest that SO₂ and NO_x emissions decreased (-3.3 and -2.0% year⁻¹, respectively) contrary to NH₃ emissions that increased slightly ($+0.2\%$ year⁻¹) over the period 1990–2002 in France. In addition, the relative contribution of HNO₃ to acidity precipitation increased by 34% over the studied period.

Acknowledgements This work was made possible by the financial support of the “Ecole des Mines de Douai,” the French Ministry of Environment and the Environmental Agency ADEME.

References

- Avila, A. (1996). Time trends in the precipitation chemistry at a mountain site in Northeastern Spain for the period 1983–1994. *Atmospheric Environment*, 30, 1363–1373.
- Charron, A., Plaisance, H., Sauvage, S., Coddeville, P., Galloo, J. C., & Guillermo, R. (1998). Intercomparison between three receptor-oriented models applied to acidic species in precipitation. *The Science of the Total Environment*, 223, 53–63.
- Charron, A., Plaisance, H., Sauvage, S., Coddeville, P., Galloo, J. C., & Guillermo, R. (2000). A study of the source-receptor relationships influencing the acidity of precipitation collected at a rural site in France. *Atmospheric Environment*, 34, 3665–3674.
- De Leeuw, F. A. A. M. (2000). Trends in ground level ozone concentrations in the European Union. *Environmental Science & Policy*, 3, 189–199.
- Fujita, S. I., Takahashi, A., Weng, J. H., Huang, L. F., Kim, H. K., Li C.K., et al. (2000). Precipitation chemistry in East Asia. *Atmospheric Environment*, 34, 525–537.
- Galloway, J. N., Likens, G. E., Keene, W. C., & Miller, J. M. (1982). The composition of precipitation in remote areas of the world. *Journal of Geophysical Research*, 87, 8771–8786.
- Gilbert, R. O. (1987). Statistical methods for environmental monitoring. Pacific Northwest Laboratory, Van Nostrand Reinhold, New York, ISBN 0-442-23050-8.
- Harrison, R. M. (1987). Acid rain – Scientific and technical advances. In R. Perry, R. M. Harrison, J. N. B. Bell, & J. N. Lester (Eds.), London: Selper Ltd.
- Hayman, G. (2004). Management and operation of the UK acid deposition monitoring network: Data summary for 2003.

- AEAT/ENV/R/1818, Department for Environment, Food and Rural affairs and the Devolved Administrations.
- Hirsch, R. M., Alexander, R. B., & Smith, R. A. (1991). Selection of methods for the detection and estimation of trends in water quality. *Water Resources Research*, 27, 803–813.
- Holland, D. M., Caragea, P., & Smith, R. L. (2004). Regional trends in rural sulfur concentrations. *Atmospheric Environment*, 38, 1673–1684.
- Hůnová, I., Šantroch, J., & Ostadnická, J. (2004). Ambient air quality and deposition trends at rural stations in the Czech Republic during 1993–2001. *Atmospheric Environment*, 38, 887–898.
- Kelly, V. R., Lovett, G. M., Weathers, K. C., & Likens, G. E. (2002). Trends in atmospheric concentration and deposition compared to regional and local pollutant emissions at a rural site in southeastern New York, USA. *Atmospheric Environment*, 36, 1569–1575.
- Kvaalen, H., Solberg, S., Clarke, N., Torp, T., & Aamlid, D. (2002). Time series study of concentrations of SO_4^{2-} and H^+ in precipitation and soil waters in Norway. *Environmental Pollution*, 117, 215–224.
- Leck, C., & Rodhe, H. (1989). On the relation between anthropogenic SO_2 emissions and concentration of sulfate in air and precipitation. *Atmospheric Environment*, 23, 959–966.
- Lehmann, C. M. B., Bowersox, V. C., & Larson, S. M. (2005). Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. *Environmental Pollution*, 135, 347–361.
- Loye-Pilot, M. D., Martin, J. M., & Morelli, J. (1986). Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. *Nature*, 321, 427–428.
- Lynch, J. A., Grimm, J. W., & Bowersox, V. C. (1995). Trends in precipitation chemistry in the United States: A national perspective, 1980–1992. *Atmospheric Environment*, 29, 1231–1246.
- Marín, E., Pérez-Amaral, T., Rúa, A., & Hernández, E. (2001). The Evolution of the pH in Europe (1986–1997) using panel data. *Chemosphere*, 45, 329–337.
- Munger, J. W. (1982). Chemistry of atmospheric precipitation in the north-central United States: Influence of sulfate, nitrate, ammonia and calcareous soil particulates. *Atmospheric Environment*, 16, 1633–1645.
- Nilles, M. A., & Conley, B. E. (2001). Changes in the chemistry of precipitation in the United States, 1981–1998. *Water, Air and Soil Pollution*, 130, 409–414.
- Plaisance, H., Coddeville, P., Guillermo, R., & Roussel, I. (1996). Spatial variability and source identification of rural precipitation chemistry in France. *The Science of the Total Environment*, 180, 257–270.
- Puxbaum, H., Simeonov, V., & Kalina, M. F. (1998). Ten years trends (1984–1993) in the precipitation chemistry in central Austria. *Atmospheric Environment*, 32, 193–202.
- Sen, P. K. (1968). Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistical Association*, 63, 1379–1389.
- Seto, S., Nakamura, A., Noguchi, I., Ohizumi, T., Fukuzaki, N., Toyama, S., et al. (2002). Annual and seasonal trends in chemical composition of precipitation in Japan during 1989–1998. *Atmospheric Environment*, 36, 3505–3517.
- Sirois, A. (1998). WMO/EMEP Workshop on Advanced Statistical Methods and their application to Air Quality Data sets. Helsinki.
- Veselý, J., Majer, V., & Norton, S. A. (2002). Heterogeneous response of central European streams to decreased acidic atmospheric deposition. *Environmental Pollution*, 120, 275–281.
- Weijers, G. T., & Vugts, H. F. (1990). The composition of bulk precipitation on a coastal island with agriculture compared to an urban region. *Atmospheric Environment*, 24, 3021–3031.
- Yue, S., & Pilon, P. (2002). Power of the Mann–Kendall and Spearman's rho tests for detecting monotonic trends in hydrological series. *Journal of Hydrology*, 259, 254–271.
- Zimmermann, F., Lux, H., & Maenhaut, W. (2003). A review of air pollution and atmospheric deposition dynamics in Southern Saxony, Germany, Central Europe. *Atmospheric Environment*, 37, 671–691.

Monitoring Long-term Trends in Sulfate and Ammonium in US Precipitation: Results from the National Atmospheric Deposition Program/National Trends Network

Christopher M. B. Lehmann · Van C. Bowersox ·
Robert S. Larson · Susan M. Larson

Received: 17 June 2005 / Revised: 23 February 2006 / Accepted: 12 March 2006 / Published online: 5 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Data from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) indicate significant changes have occurred in precipitation chemistry and the chemical climate in the United States (US). A Seasonal Kendall Trend (SKT) analysis shows statistically significant increases in precipitation ammonium concentrations at 64% of 159 continental US NADP/NTN sites evaluated from Winter 1985 to Fall 2004 (Dec. 1984 – Nov. 2004). Sulfate decreases were widespread, with an SKT analysis indicating statistically significant decreases at 89% of sites evaluated. Ratios of chemical equivalent concentrations of ammonium to sulfate in precipitation have risen to the extent that

ammonium now exceeds sulfate over more than half of the continental U.S. on a precipitation-weighted-mean annual basis. These trends in the concentrations of ammonium, sulfate, and other species have been accompanied by significant decreases in the frequency of acidic precipitation ($\text{pH} < 5.0$) in the last decade.

Keywords chemical climate · precipitation chemistry · trend analysis

1 Introduction

Trends in precipitation chemistry indicate changes in air quality and the chemical climate of the Earth's atmosphere. Since precipitation scavenges airborne gases and particles, trends in air quality and precipitation chemistry are related. Such trends represent the combined effects of natural and human-induced pollutant emissions, physical and chemical transformations, and climate. Long-term precipitation chemistry measurements are a resource for examining these changes.

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) has measured the concentrations of acids, nutrients, and base cations in weekly United States (US) precipitation samples for more than two decades to characterize the chemical climate of the US and its temporal and spatial trends (Lamb & Bowersox, 2000). NADP/

C. M. B. Lehmann (✉) · V. C. Bowersox · R. S. Larson
National Atmospheric Deposition Program,
Illinois State Water Survey,
2204 Griffith Dr.,
Champaign, IL 61820-7495, USA
e-mail: clehmann@uiuc.edu

V. C. Bowersox
e-mail: sox@sws.uiuc.edu

R. S. Larson
e-mail: blarson@uiuc.edu

S. M. Larson
Department of Civil and Environmental Engineering,
University of Illinois,
206 Engineering Hall, MC-272, 1308 W. Green St.,
Urbana, IL 61801, USA
e-mail: smlarson@uiuc.edu

NTN reported measurements include concentrations of sulfate, nitrate, chloride, ammonium, potassium, sodium, calcium, and magnesium, as well as pH and specific conductivity (National Atmospheric Deposition Program (NADP), 2005).

This study focuses on trends in ammonium and sulfate concentrations in precipitation and their resulting influence on precipitation pH. Ammonium deposition from precipitation is of interest because ammonium is a nutrient that stimulates plant growth in nitrogen-limited systems (Walker, Aneja, & Dickey, 2000). While ammonium deposition can promote crop growth, it also can alter the structure and diversity of native plant communities (Krupa, 2003). Sulfate contributes to acidic deposition (i.e., precipitation $\text{pH} < 5.0$), leading to adverse impacts in acid-sensitive ecosystems (Sisterson, Bowersox, & Olsen, 1990; Stoddard et al., 2003), although sulfate deposition contributes to the sulfur requirements of some agricultural crops (Knights, Zhao, Spiro, & McGrath, 2000).

The chemical equivalent ratios of ammonium to sulfate in precipitation ($[\text{NH}_4 \text{ eq.}]/[\text{SO}_4 \text{ eq.}]$) are an indicator of which ammonium/sulfur species dominates in the atmospheric aerosol phase. Considering an aerosol system where the dominant reactive species are ammonium and sulfate, ammonium will preferentially react with sulfate to form (in turn) ammonium bisulfate (NH_4HSO_4) ($[\text{NH}_4 \text{ eq.}]/[\text{SO}_4 \text{ eq.}] = 0.50$), letovicite ($\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ($[\text{NH}_4 \text{ eq.}]/[\text{SO}_4 \text{ eq.}] = 0.75$), and ammonium sulfate ($\text{NH}_4)_2\text{SO}_4$ ($[\text{NH}_4 \text{ eq.}]/[\text{SO}_4 \text{ eq.}] = 1.00$), depending on the relative amount of ammonium available (Seinfeld & Pandis, 1998). Under typical atmospheric conditions, these sub-micrometer aerosol species are relatively stable, and can be transported long distances. When the ammonium in the atmosphere exceeds that required to form ammonium sulfate (i.e., $[\text{NH}_4 \text{ eq.}]/[\text{SO}_4 \text{ eq.}] > 1.00$), there exists an “ammonia rich” condition in which ammonium is available to react with other species. For example, ammonium can react with nitrate to form ammonium nitrate, NH_4NO_3 (Seinfeld & Pandis, 1998). Ammonium nitrate is a labile species that partitions between gas and aerosol phases depending on temperature and gas-phase concentrations of nitric acid and ammonia, and because of its reactivity, is more likely to be scavenged and deposited locally. Modeling results indicate that when NO_x and SO_2 emissions are reduced in relation to

ammonia emissions, NH_3 remains in the reactive gas phase, significantly reducing the transport distance, leading to local deposition (Hov, Hjollo, & Eliassen, 1994).

The present study evaluates trends in ammonium and sulfate concentrations in precipitation using the Seasonal Kendall Trend (SKT) test. The SKT test is a non-parametric hypothesis test based on Kendall's tau statistic, and is useful for evaluating trends in environmental data where the underlying distribution is unknown (Gilbert, 1987; Helsel & Hirsch, 1992). The SKT is an extension of the Kendall Trend test and accounts for seasonal variations (seasonality) in data by comparing the same period of the year over time; i.e., trends in spring concentrations and summer concentrations are treated separately (Gilbert, 1987; Helsel & Hirsch, 1992).

2 Methodology

Data from the NADP/NTN are available on the Internet at <http://nadp.sws.uiuc.edu/NTN>. Only samples flagged as valid by the NADP were used in the trend analysis. Valid samples are those collected following standard procedures and not flagged as being significantly contaminated (NADP, 2005). For January 1984–December 2004, data from 159 continental US NADP/NTN sites met or exceeded defined data completeness criteria (Lehmann, Bowersox, & Larson, 2005).

For the SKT analyses, statistical seasons were based on meteorological seasons (December–February = winter, etc.) and divided into high and low sample volume classes, resulting in eight statistical seasons per year (Lehmann et al., 2005). The high sample volume class includes samples with volumes at or above the seasonal median sample volume. The low sample volume class includes samples with volumes below the seasonal median sample volume. Applying this approach identified more statistically significant trends in precipitation chemistry when compared to evaluating trends on an annual or a meteorological season basis (Lehmann et al., 2005). The SKT analyses were performed for the period Winter 1985–Fall 2004 (Dec. 1984–Nov. 2004) using the EnvironmentalStats version 2.0 package of S-PLUS 6.1 (Millard & Neerchal, 2000). The null hypotheses were that the trend is zero (Kendall's tau

statistic=0) and that the seasonal taus were homogeneous (differences in Kendall's tau values were statistically insignificant) over all statistical seasons. The statistical significance level was set at 90% for evaluation of trend ($p \leq 0.10$) and seasonal homogeneity ($p > 0.10$). The magnitude of the trend slope was determined by taking the Sen's median estimator of the natural log of the concentration data in units of $\mu\text{eq/l}$. The Sen's median estimator of log-transformed concentrations provides a non-parametric estimate of the percent change of concentration over the period of interest (Gilbert, 1987; Helsel & Hirsch, 1992; Millard & Neerchal, 2000). The median trend for all 159 sites evaluated was calculated to represent the overall national trend.

In addition to the SKT analysis, changes in equivalent ratios of ammonium to sulfate and the frequency of acidic precipitation were determined. Equivalent ratios of precipitation ammonium to sulfate concentrations were calculated on a three-year precipitation-weighted-mean basis. The frequency of acidic precipitation was determined from weekly events over this three year period, with acidic precipitation defined as samples having a $\text{pH} < 5.0$ (Seinfeld & Pandis, 1998). All isopleth contour maps in this study were created using an Inverse-Distance-Weighted (IDW) algorithm based on all 2.5 km grid cells within 500 km of NADP/NTN sites (Lehmann et al., 2005). A linear IDW fit was used for trend maps, and a cubic IDW fit was used for ammonium to sulfate ratio maps and acidic precipitation frequency maps. The relative continental U.S. area contained in each isopleth contour class was calculated from the number of grid cells contained in each class.

3 Results and Discussion

3.1 Trends in Ammonium and Sulfate Concentrations in Precipitation

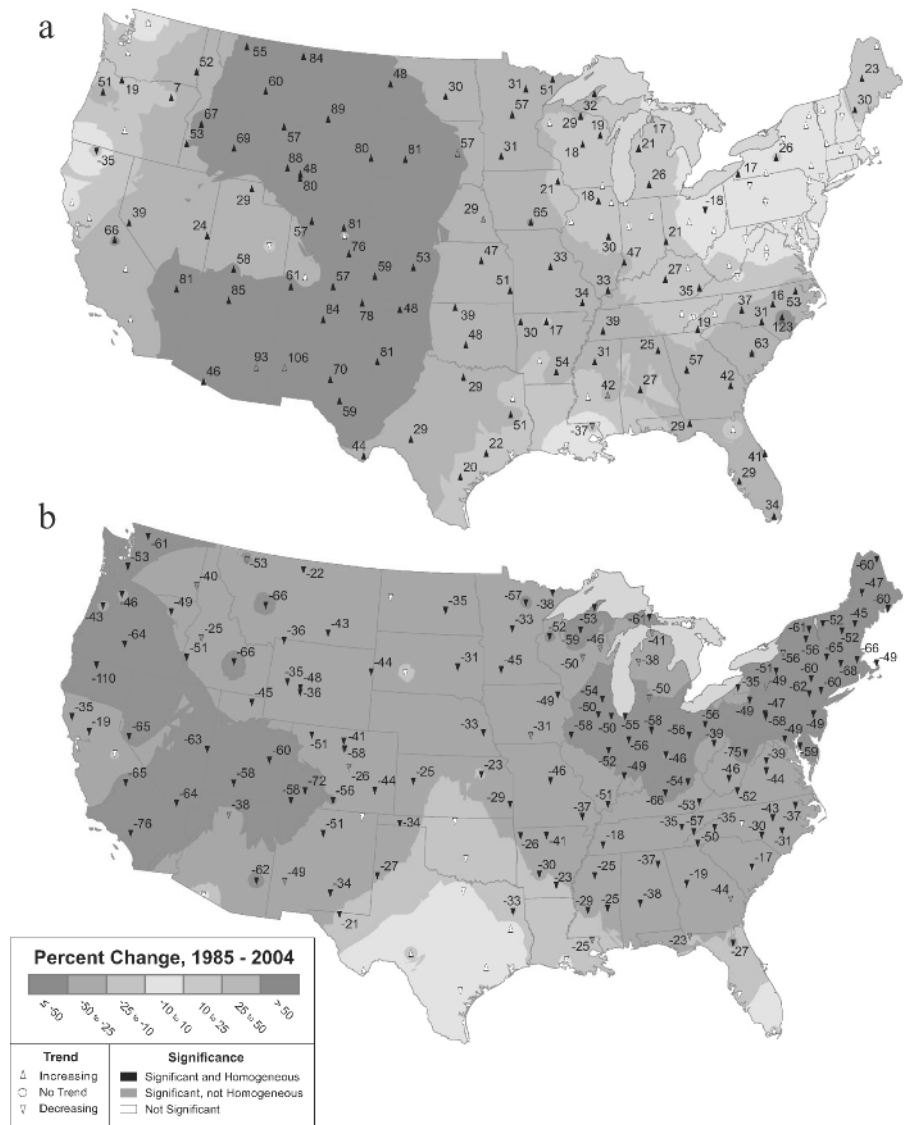
Significant increases in ammonium concentrations in precipitation were observed across most of the continental US over the 20-year period from Winter 1985 to Fall 2004 (Table 1, Fig. 1a). Trends were found to be increasing and statistically significant at 101 (64%) of the 159 sites evaluated, with most of these trends (95 sites, 60%) being statistically significant and homogeneous across seasons. Statistically significant decreasing trends were found at only three sites (2%), with two of these trends (1%) being statistically significant and homogeneous. The few sites with decreasing trends were predominately along the coasts, and trends decreasing by more than 10% in magnitude represented less than 1% of the area of the continental US. Trends increasing by more than 50% in magnitude represented 30% of the US and were spread over a large area in the central part of the country. The largest magnitude increase (+123%) occurred in southeastern North Carolina, where Walker et al. (2000) have reported large ammonium increases related to swine population growth.

The median ammonium trend across the 159 sites evaluated was +28.5% (Table 1). In the US, estimates of ammonia emissions are limited (and existing emissions inventories from the US EPA do not begin until 1990 (United States Environmental Protection Agency (U.S. EPA), 2005)), so it is difficult to compare trends in ammonium precipitation with ammonia emissions. However data from the US EPA indicate that ammonia emissions may have

Table 1 Seasonal Kendall trend test of NTN concentrations, Winter 1985–Fall 2004

Median national trend (Sen's estimator) %	Increasing precipitation concentration trend						Decreasing precipitation concentration trend					
	Total sites		Statistically significant trend ($p \leq 0.10$)		Statistically significant & homogeneous trend ($p > 0.10$)		Total sites		Statistically significant trend ($p \leq 0.10$)		Statistically significant & homogeneous trend ($p > 0.10$)	
	Number	%	Number	%	Number	%	Number	%	Number	%	Number	%
NH ₄ +28.5	142	89%	101	64%	95	60%	17	11%	3	2%	2	1%
SO ₄ -45.7	5	3%	0	0%	0	0%	154	97%	141	89%	124	78%

Fig. 1 Trend significance ($p \leq 0.10$), trend homogeneity ($p > 0.10$), and percent change (Sen's estimator) from Winter 1985 to Fall 2004 for **a** ammonium concentration and **b** sulfate concentration. Numeric values indicated at sites with a significant trend



dropped since 2000 (United States Environmental Protection Agency (U.S. EPA), 2005), in contrast to the measured ammonium trends in precipitation.

Sulfate concentrations decreased over nearly the entire continental US from Winter 1985 to Fall 2004 (Table 1, Fig. 1b). Statistically significant decreases occurred at 141 of the 159 sites in this study (89%), with the majority of decreasing trends (124 sites, 78%) being statistically significant and homogeneous. Sulfate concentration increases were confined to Texas and southern Florida, representing less than 1% of the continental US, and none of the increases was statistically significant. Elsewhere, sulfate decreases were 10% or more with 25 to >50%

reductions throughout most of the western and northeastern US (The decrease of >100% in northern California is an aberration of the Sen's median estimator. The 90th percentile confidence interval at this site extends from -130 to -86%.)

The median sulfate trend across the 159 sites evaluated was -45.7% (Table 1). Other researchers have reported sulfate decreases similar to those observed in this study, particularly in the northeastern U.S. where sulfur dioxide emissions reductions have occurred (Civerolo & Rao, 2001; Lynch, Bowersox, & Grimm, 2000; Nilles & Conley, 2001). Other researchers (Malm, Schichtel, Ames, & Gebhart, 2002) also have observed sulfate increases in Texas,

Fig. 2 Three-year precipitation-weighted-mean ammonium to sulfate chemical equivalent ratios for **a** 1984–1986, **b** 1994–1996, and **c** 2002–2004

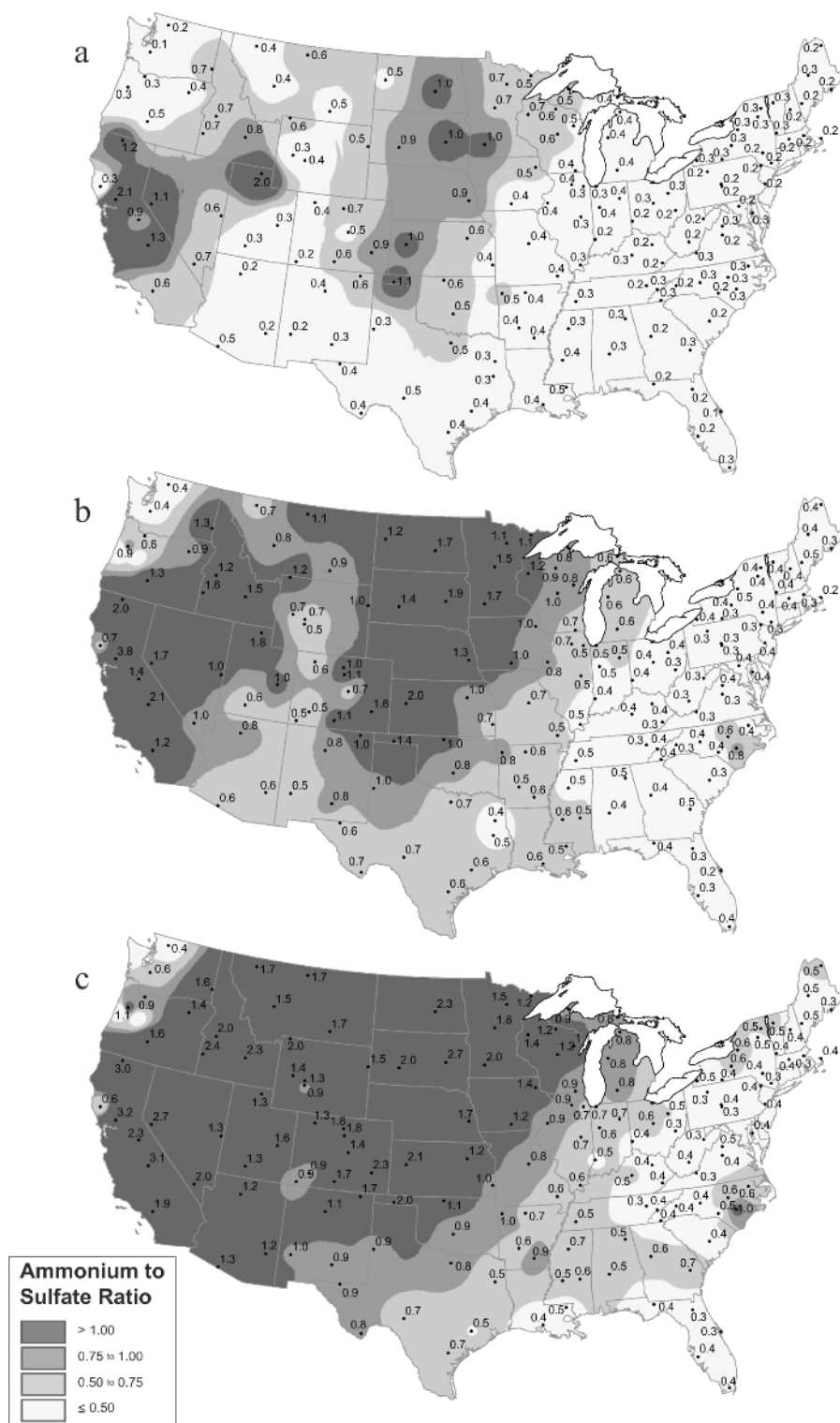
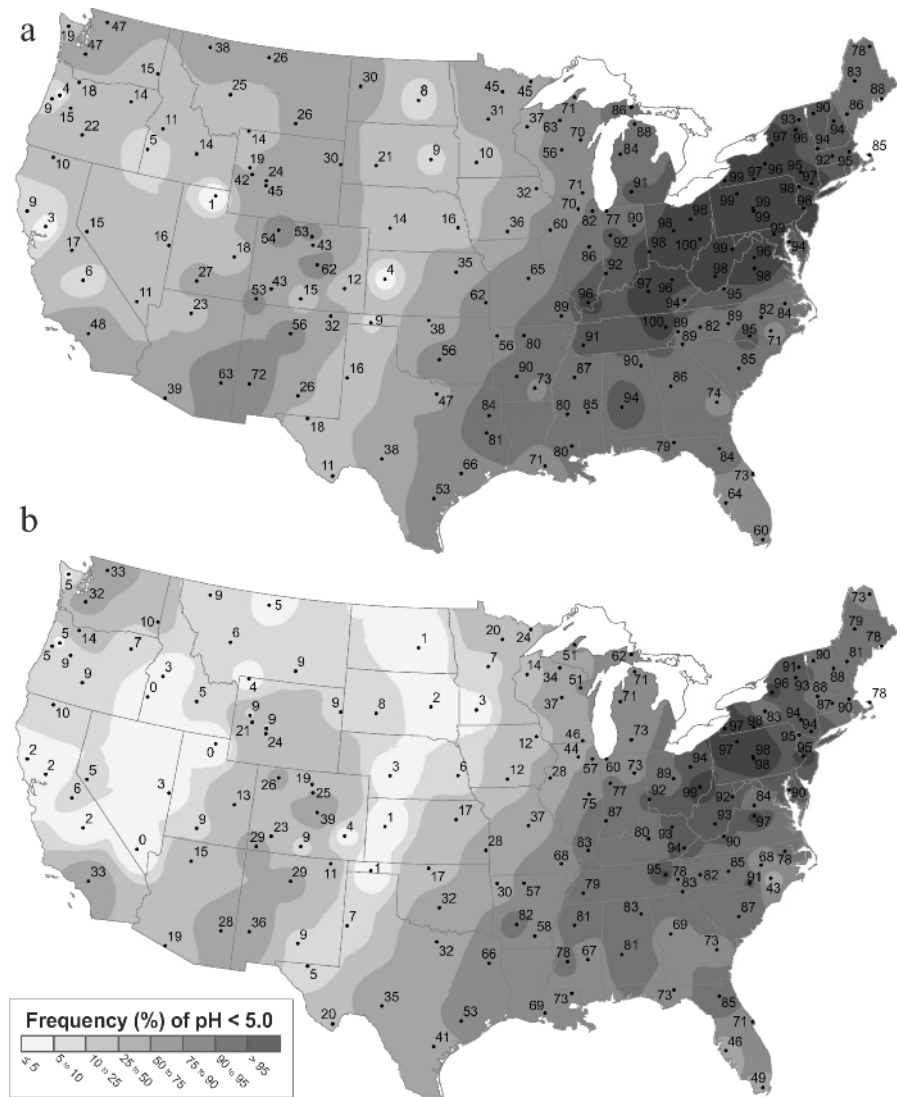


Fig. 3 Three-year frequency of occurrence of acidic precipitation ($\text{pH} < 5.0$) for **a** 1994–1996 and **b** 2002–2004



which they attributed to sulfur dioxide emission increases from 1988 to 1998 in the southwestern US. Transport of pollutants from outside the US may also be a factor. However, sulfur dioxide emissions trends data are not available to confirm this supposition.

3.2 Changes in the Ammonium to Sulfate Equivalent Ratio

The resulting impact of increasing ammonium trends accompanied by decreasing sulfate trends is demonstrated by the ammonium to sulfate equivalent ratio. Three-year precipitation-weighted-mean ammonium to sulfate equivalent ratios were calculated for Jan. 1984–Dec. 1986 (Fig. 2a), Jan. 1994–Dec. 1996

(Fig. 2b), and Jan. 2002–Dec. 2004 (Fig. 2c). From 1984 to 1986, ammonium to sulfate ratios were less than 0.5 for more than half of the continental US (Fig. 2a). Ammonia-rich regions ($[\text{NH}_4 \text{ eq.}]/[\text{SO}_4 \text{ eq.}] > 1.00$) were less than 10% of the US. For the period 1994–1996, regions with an ammonium to sulfate ratio less than 0.5 constituted approximately 24% of the US, and ammonium to sulfate ratios exceeded 1.0 in approximately 34% of the US (Fig. 2b). For the period 2002–2004, ammonium to sulfate ratios were less than 0.5 in only 16% of the US. In these regions, the influence of sea salt sulfate is a likely contributor. Ammonium to sulfate ratios exceeding 1.0 were found in over half of the U.S., corresponding to regions with significant ammonium

concentration increases (Fig. 1a). In these ammonia-rich regions, it is likely that ammonium nitrate and ammonia gas scavenged by precipitation have contributed to the upward trends in ammonium concentrations in precipitation, leading to local deposition of ammonium.

3.3 Frequency of Acidic Precipitation, 1994–1996 vs. 2002–2004

The frequency of acidic precipitation was evaluated for two 3-year periods, Jan. 1994–Dec. 1996 (Fig. 3a) and Jan. 2002–Dec. 2004 (Fig. 3b). The 1984–1986 trend maps were not included in this part of the study, because the NADP/NTN instituted a sample protocol change in 1994 to eliminate a sampling artifact inherent in prior determinations of sample pH in certain regions (National Atmospheric Deposition Program (NADP), 1995). (Precipitation concentrations presented in Fig. 2a, were not affected by the sampling artifact.) For the period 1994–1996, acidic precipitation occurred in more than half of precipitation samples measured over approximately 40% of the continental US. At least 1% of samples at all sites had a $\text{pH} < 5.0$. The highest incidence of acidic precipitation occurred in the northeastern US, with areas in eastern Ohio, Pennsylvania, and surrounding regions having acidic precipitation in virtually all samples. For the years 2002–2004, the area where more than half of the samples with $\text{pH} < 5.0$ decreased to 35%. In this period, three sites in the western US experienced virtually no acidic precipitation. The highest incidence of acidic precipitation remained centered in the northeast, although the incidence of acidic precipitation decreased overall. This change in acidic precipitation frequency is due to the combined effects of increased ammonium, decreased sulfate, and trends in other precipitation species noted in our previously published work (Lehmann et al., 2005), including decreased nitrate and increased buffering capacity from earth crustal cations.

The greatest decrease in precipitation acidity occurred in states surrounding Lakes Superior and Michigan. Only six sites studied experienced an increase in the frequency of acidic precipitation between the two time periods. Although the reduced frequency of acidic precipitation mitigates the chronic effects of ecosystem exposure, the majority of the US

continues to experience acidic precipitation to some extent.

4 Summary

Data from the National Atmospheric Deposition Program/National Trends Network indicate that statistically significant trends have occurred over the twenty-year period from Winter 1985 to Fall 2004 for ammonium and sulfate concentrations in precipitation. Trends in ammonium, sulfate, and other species have led to a decrease in the frequency of acidic precipitation ($\text{pH} < 5.0$) in the continental US, although the majority of the US continues to experience acidic precipitation at some frequency.

Increases in ammonium concentrations in precipitation and ammonium wet deposition were observed across most of the continental United States, with a median trend across the 159 sites evaluated of +28.5%. Increases were particularly notable in the central and upper Midwest. Only limited ammonia emissions trends data are available from the US EPA for comparison (indicating a need for more detailed ammonia emissions inventories), but those available indicate that changes in emissions alone cannot account for observed ammonium increases. These findings point to the need for routine air concentration measurements of gas-phase ammonia, a gas constituent not routinely measured in the US, so that we can better understand the relationships between ammonia emissions, gaseous ammonia, particulate ammonium, and ammonium in precipitation.

Sulfate concentrations in precipitation and wet deposition decreased markedly in nearly the entire continental US over the trend analysis period. Sulfate concentration increases were confined to Texas and southern Florida, although no increasing trends were statistically significant. The national trend in precipitation sulfate was -45.7% , consistent with decreasing sulfur dioxide emissions trends reported in the literature. Trends in ammonium and sulfate have resulted in ammonium to sulfate equivalent ratios exceeding 1.0, creating an ammonia-rich environment for more than half of the US from 2002–2004. This change has likely reduced the transport distance of ammonium, indicating that trends in ammonium may be most influenced by local emissions sources.

Trends observed in precipitation chemistry and wet deposition are a manifestation of changes in the chemical climate of the atmosphere in the US, only some of which appear to be attributable to changes in emissions. Because trends in pollutant species are linked, there is a need for continued research into multi-constituent emission relationships. There is also a continued need for long-term monitoring of precipitation chemistry to evaluate the impact of emissions regulations on the chemical climate of the atmosphere.

Acknowledgements The NADP is National Research Support Project-3: A Long-term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 240 sponsors support the NADP, including State Agricultural Experiment Stations; universities; private companies and other non-governmental organizations; Canadian government agencies; state, local, and tribal government organizations; and federal agencies, including the US Department of Agriculture-Cooperative State Research, Education, and Extension Service (under agreement no. 2002-39138-11964). Any findings or conclusions in this article do not necessarily reflect the views of the US Department of Agriculture or other sponsors.

References

- Civerolo, K., & Rao, S. T. (2001). Space-time analysis of precipitation-weighted sulfate concentrations over the eastern US. *Atmospheric Environment*, 35, 5657–5661.
- Gilbert, R. O. (1987). *Statistical methods in environmental pollution monitoring*. New York: Van Nostrand Reinhold, pp. 225–240.
- Helsel, D. R., & Hirsch, R. M. (1992). *Statistical methods in water resources, U.S.* (pp. 338–340). Reston, VA: Geological Survey.
- Hov, O., Hjollo, B. A., & Eliassen, A. (1994). Transport distance of ammonia and ammonium in northern Europe: I. Model description. *Journal of Geophysical Research Atmospheres*, 99, 18735–18748.
- Knights, J. S., Zhao, F. J., Spiro, B., & McGrath, S. P. (2000). Long-term effects of land use and fertilizer treatments on sulfur cycling. *Journal of Environmental Quality*, 29, 1867–1874.
- Krupa, S. V. (2003). Effects of atmospheric ammonia (NH₃) on terrestrial vegetation: A review. *Environmental Pollution*, 124, 179–221.
- Lamb, D., & Bowersox, V. (2000). The national atmospheric deposition program: An overview. *Atmospheric Environment*, 34, 1661–1663.
- Lehmann, C. M. B., Bowersox, V. C., & Larson, S. M. (2005). Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. *Environmental Pollution*, 35, 347–361.
- Lynch, J. A., Bowersox, V. C., & Grimm, J. W. (2000). Changes in sulfate deposition in eastern USA following implementation of phase I of title IV of the clean air act amendments of 1990. *Atmospheric Environment*, 34, 1665–1680.
- Malm, W. C., Schichtel, B. A., Ames, R. B., & Gebhart, K. A. (2002). A 10-year spatial and temporal trend of sulfate across the United States. *Journal Geophysical Research*, 107, 4627–4646.
- Millard, S. P., & Neerchal, N. K. (2000). *Environmental statistics with S-Plus* (pp. 680–685). Boca Raton: CRC.
- National Atmospheric Deposition Program (NADP) (1995). Notification of important change in NADP/NTN procedures on 11 January 1994. Illinois State Water Survey, Champaign, IL, U.S.A., <http://nadp.sws.uiuc.edu/documentation/advisory.html>, accessed 16 January 2006.
- National Atmospheric Deposition Program (NADP) (2005). National trends network. Illinois State Water Survey, Champaign, IL, U.S.A., <http://nadp.sws.uiuc.edu/NTN>, accessed 16 January 2006.
- Nilles, M. A., Conley, B. E. (2001). Changes in the chemistry of precipitation in the United States, 1981–1998. *Water, Air, and Soil Pollution*, 130, 409–414.
- Seinfeld, J. H., & Pandis, S. N. (1998). *Atmospheric chemistry and physics: From air pollution to climate change* (pp. 529–531, 1030–10330). New York: Wiley.
- Sisterson, D. L., Bowersox, V. C., & Olsen, A. R. (1990). *Wet deposition of atmospheric pollutants*. National Acid Precipitation Assessment Program, Washington, D.C., U. S.A., 6–39 to 6–222 and 6–A1 to 6–A46.
- Stoddard, J. L., Kahl, J. S., Deviney, F. A., DeWalle, D. R., Driscoll, C. T., Herlihy, A. T., et al. (2003). *Response of surface water chemistry to the clean air act amendments of 1990*. United States Environmental Protection Agency, Research Triangle Park, NC, U.S.A., pp. 78.
- United States Environmental Protection Agency (U.S. EPA) (2005). 1970–2002 Average annual emissions, all criteria pollutants. Washington, D.C., <http://www.epa.gov/ttn/chief/trends/index.html>, accessed January 16, 2006.
- Walker, J. T., Aneja, V. P., & Dickey, D. A. (2000). Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmospheric Environment*, 34, 3407–3418.

Temporal Trends of Non-sea Salt Sulfate and Nitrate in Wet Deposition in Japan

Izumi Noguchi • Kentaro Hayashi •
Masahide Aikawa • Tsuyoshi Ohizumi •
Yukiya Minami • Moritsugu Kitamura •
Akira Takahashi • Hiroshi Tanimoto •
Kazuhide Matsuda • Hiroshi Hara

Received: 12 June 2005 / Accepted: 8 May 2006 / Published online: 3 March 2007
© Springer Science + Business Media B.V. 2007

Abstract Temporal trends of non-sea salt (nss-) sulfate and nitrate were analyzed from nationwide precipitation chemistry measurements provided by the Ministry of the Environment (MOE) for the 1988–2002 fiscal years (April–March). The concentrations and deposition of nss-sulfate were found to be decreasing, and those of nitrate were stable or slightly increasing at most sites. These deposition trends were discussed from the viewpoint of emissions of SO₂ and

NO_x during the period of interest. Because monitoring techniques have changed in the number of active sites, samplers, and analytical methods during the operation period, the median of all annual depositions measured in Japan in a specific year was selected as the annual representative. The contribution of specific emission sources was also calculated for 1990 on the basis of the nss-sulfate and nitrate deposition in Japan obtained with a model simulation in which the model

I. Noguchi (✉)
Hokkaido Inst. of Environ. Sciences,
Kita 19 Nishi 12, Kita-ku,
Sapporo 060-0819, Japan
e-mail: izumi@hokkaido-ies.go.jp

K. Hayashi
National Institute for Agro-Environmental Sciences,
3-1-3 Kannondai,
Tsukuba 305-8604, Japan

M. Aikawa
Hyogo Prefectural Institute of Public Health and
Environmental Sciences,
3-1-27 Yukihiro Suma-ku, Kobe,
Hyogo 654-0037, Japan

T. Ohizumi
Acid Deposition and Oxidant Research Center,
1182 Sowa, Niigata-shi 950-2144, Japan

Y. Minami
Ishikawa Prefectural University,
1-308 Suematsu, Nonouchi,
Ishikawa 921-8836, Japan

M. Kitamura
Ishikawa Prefectural Institute of Public Health and
Environmental Science,
1-11 Taiyogaoka, Kanazawa,
Ishikawa 920-1154, Japan

A. Takahashi
Central Research Institute of Electric Power Industry,
1646 Abiko, Abiko,
Chiba 270-1194, Japan

H. Tanimoto
National Institute for Environmental Studies,
16-2 Onogawa, Tsukuba,
Ibaraki 305-8506, Japan

K. Matsuda
Meisei University,
2-1-1 Hodokubo, Hino,
Tokyo 191-8506, Japan

H. Hara
Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu,
Tokyo 183-8509, Japan

did not include volcanic emissions from Mt. Oyama, Miyakejima Island, which began to erupt suddenly and violently in 2000. For nss-sulfate, the calculated deposition agrees well with the intensity and trends of the median up to 1999. After 2000, a higher deposition than calculated in the preceding years was evident, which is attributable to the volcanic SO_2 from Mt. Oyama. For nitrate, both the calculated and observed depositions were slightly increasing; however, the calculation was found to exceed the observation.

Keywords Acid deposition · Temporal trend · Sulfate · Nitrate · Long-range transport

1 Introduction

The trend analysis for the concentration and deposition of non-sea salt sulfate and nitrate ($\text{nss} - \text{SO}_4^{2-}$ and NO_3^-) in precipitation will provide a basis for estimating the integrated effects on the terrestrial ecosystem and discussing the relationships between precursor emissions and acid depositions. These relationships play an important role in predicting the acid deposition and its effects.

In western Japan, an increasing trend in the ratio of NO_3^- to $\text{nss} - \text{SO}_4^{2-}$ was observed from 1987 through 1996 (Takahashi and Fujita 2000). Moreover, Seto et al. (2002) analyzed the long-term trends and seasonal variations for the $\text{nss} - \text{SO}_4^{2-}$, NO_3^- , NH_4^+ , and $\text{nss} - \text{Ca}^{2+}$ concentrations in precipitation chemistry datasets collected by the Ministry of the Environment (MOE) during 1989–1998. However, no details of the relationships between the concentrations and depositions of $\text{nss} - \text{SO}_4^{2-}$ and NO_3^- and the trends in the emissions of SO_2 and NO_x were given. In addition, Calori et al. (2001) simulated the long-term trends for $\text{nss} - \text{SO}_4^{2-}$ depositions using an ATMOS model from 1985 through 1997. Their results indicated an increasing trend of $\text{nss} - \text{SO}_4^{2-}$ depositions in Japan. However, the observed $\text{nss} - \text{SO}_4^{2-}$ deposition in Japan was not increasing during 1990s. The discrepancy would be attributed to the two points: the SO_2 emission in China did not increase as calculated, and the emission from volcanoes fluctuated much more than projected.

In this study, temporal changes in the deposition of $\text{nss} - \text{SO}_4^{2-}$ and NO_3^- in precipitation chemistry datasets from fiscal years (April–March) 1988

through 2002 provided by the MOE (JADS) were studied in terms of anthropogenic emissions and volcanic emissions.

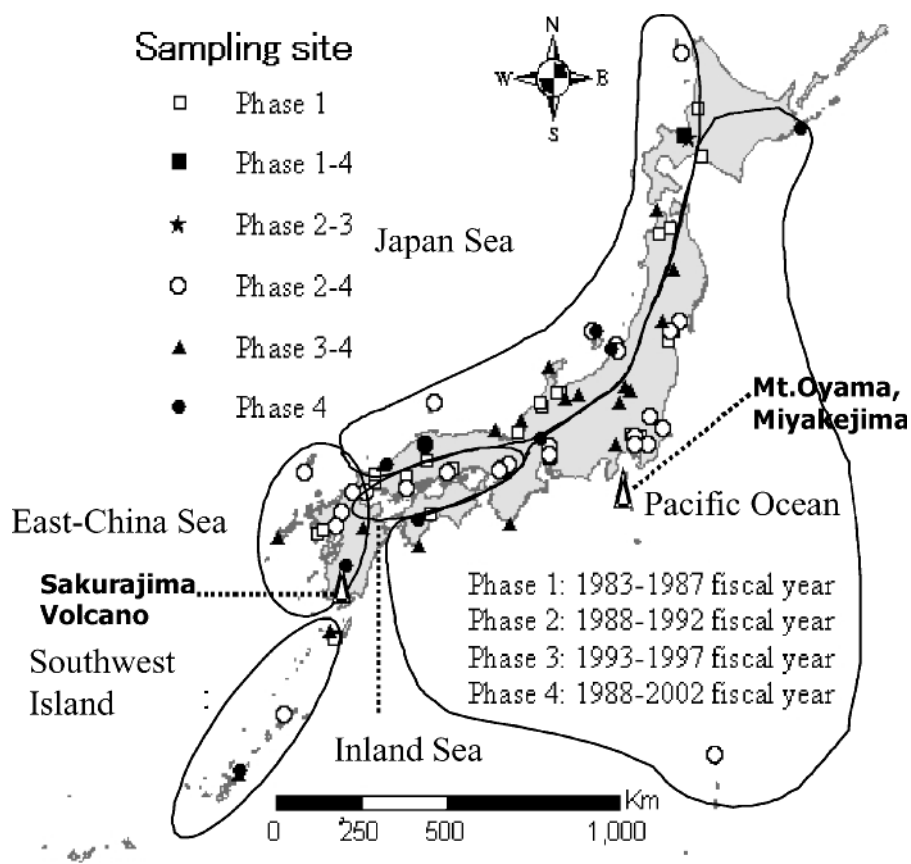
2 Dataset and Methods

The monitoring network, JADS, has been in operation since FY 1973 using bulk samplers (Phase 1). After that, JADS was composed of as many as 32–54 stations on a national scale with wet-only samplers with rain-sensors since FY 1988 (Fig. 1). The MOE reported the $\text{nss} - \text{SO}_4^{2-}$ and NO_3^- temporal trend at each site for each measurement period as shown in Table 1 (Hayashi et al. 2005, 2006). Temporal trend rates were calculated from the linear-regressions of monthly means. The following criteria for data selection have been applied:

- (1) The data completeness for monthly data exceeds 80%.
- (2) Each analytical result with flags for appreciable contamination was excluded for the present trend analysis.
- (3) Annual change rates were not evaluated for data less than four years old.

Acid deposition has a focus of society because of its potential impact on ecosystems where the load is evaluated in terms of deposition. Deposition is the downward flux of materials from the atmosphere to the earth's surface, while emission is the upward flux of materials from the surface to the atmosphere. Therefore, when discussing the trend analysis, we estimated that it is better to focus on the emission along with the deposition.

In the quantitative analysis for the relationships between precursor emissions and $\text{nss} - \text{SO}_4^{2-}$ and NO_3^- depositions in the present paper, the median of annual deposition throughout Japan was selected as the annual representative and quantitative measure as shown in Table 2, because JADS datasets had different sampling frequencies for daily, weekly, biweekly, and monthly readings and because the sampling site and devices were also changed annually (Phases 2–4). The medians of annual $\text{nss} - \text{SO}_4^{2-}$ depositions were decreasing until 1999, although the medians of annual precipitation amounts were slightly increasing. On the other hand, the medians of annual

Fig. 1 Sampling sites

NO_3^- depositions are slightly increasing like the medians of annual precipitation amounts.

3 Results and Discussion

3.1 Precursor Emissions

The results from Ikeda and Higashino (1997) agreed very well with a set of observations on a national scale concerning sulfate and nitrate, which led us to apply the simulation of the emissions of sulfur dioxide and nitrogen oxides to this region. The relative contribution of each emission source was applied to the deposition in Japan. On the basis of these contributing factors, we estimated the deposition for some of the following years in accordance with the projections of both emissions. In other words, the estimate was based on the relative contributions for 1900, which was designated as the initial condition.

Ikeda and Higashino (1997) estimated that the most important emissions of $\text{nss} - \text{SO}_4^{2-}$ and NO_3^- in

precipitation are anthropogenic SO_2 and NO_2 emissions in Japan, China, and South Korea. In addition, volcanoes in Japan were also estimated to be important sources of emissions for $\text{nss} - \text{SO}_4^{2-}$. In the present context, the emissions were divided into three major categories: domestic anthropogenic sources, continental anthropogenic sources, and volcanic sources in Japan.

The emission sums from volcanoes in Japan is largest in the world. Fujita et al. (1992) estimated the emission rate of SO_2 from volcanoes in 1988 in Japan. Their results showed that the SO_2 emission from the Sakurajima volcano was the largest (50% of the total). In addition, the SO_2 emission from the Sakurajima volcano was considered to be responsible for most of the effects of $\text{nss} - \text{SO}_4^{2-}$ because the volcano is located upwind in southwest Japan on Kyushu Island. In this study, the SO_2 emission from the volcano was calculated by the results of Fujita et al. (1992) and the SO_2 emission index from the Sakurajima volcano (Ministry of the Environment, 2004). The results indicated that SO_2 emissions from

Table 1 Temporal trends for nss-sulfate and nitrate for each site and measurement period in Japan (Ministry of the Environment 2004)

Site	Area	Classification	Measurement period		Mean of annual deposition and concentration				Annual change rate			
					Start year and month		End year and month		nss – SO ₄ ²⁻ NO ₃ ⁻		nss – SO ₄ ²⁻ NO ₃ ⁻	
									mmol m ⁻² y ⁻¹ µeq L ⁻¹		mmol m ⁻² y ⁻¹ µeq L ⁻¹	
Rishiri	Japan Sea	Remote	91 Apr	98 Mar	9.2	7.8	13.4	11.3	0.23	72	0.26	72
			98 Apr	03 Mar	12.6	11.5	15.8	14.9	0.67	39	-0.38	40
Sapporo	Japan Sea	Urban	88 Apr	94 Mar	18.5	10.7	22.1	12.9	0.55	68	0.52	68
			94 Apr	03 Mar	15.6	11.8	15.4	11.7	-0.02	106	0.36	106
Nopporo	Japan Sea	Rural	88 Apr	94 Mar	Invalid data for bulk sampling in winter.							
			94 May	98 Mar	10.5	8.2	10.5	8.2	-	-	-	-
Tappi	Japan Sea	Remote	94 Apr	03 Mar	15.0	16.8	14.2	15.6	0.04	88	0.07	92
Obanazawa	Japan Sea	Eco.	94 Apr	03 Mar	17.4	19.8	11.2	13.0	0.11	98	-0.05	98
Sado	Japan Sea	Remote	91 Apr	99 Mar	22.5	22.8	14.8	15.0	-0.25	90	0.03	91
Niigata	Japan Sea	Urban	88 Apr	03 Mar	29.6	20.8	21.2	14.8	-0.17	175	0.30	175
Niitsu	Japan Sea	Rural	88 Apr	94 Mar	30.7	24.7	18.5	14.9	-0.81	67	0.33	67
			94 Apr	00 Mar	31.5	33.5	15.7	16.6	-0.07	71	0.46	71
Wajima	Japan Sea	Remote	94 Apr	03 Mar	35.0	36.1	16.8	17.2	-0.08	103	-0.01	103
Happou	Japan Sea	Remote	94 Apr	03 Mar	20.9	19.8	9.7	9.2	-0.01	87	-0.06	87
Tateyama	Japan Sea	Eco.	94 Apr	03 Mar	39.9	40.2	13.5	13.6	0.31	92	0.15	92
Echizen-cape	Japan Sea	Remote	95 Apr	03 Mar	33.0	39.6	16.8	20.1	0.26	90	0.06	90
Oki	Japan Sea	Remote	91 Apr	98 Mar	19.5	21.3	15.9	16.6	0.07	77	0.68	76
			98 Apr	03 Mar	18.3	22.0	13.0	15.4	1.40	41	0.69	51
Kyoto-Yasakae	Japan Sea	Eco.	94 Apr	03 Mar	37.7	38.0	16.6	16.8	0.03	95	0.06	95
Matsue	Japan Sea	Urban	88 Apr	01 Mar	24.1	22.5	15.3	14.4	-0.80	147	-0.12	147
			01 Mar	03 Mar	25.6	32.3	15.5	19.7	-	-	-	-
Masuda	Japan Sea	Eco.	94 Apr	99 Mar	22.3	25.2	15.4	17.3	0.05	55	0.12	55
Hachimantai	Pacific ocean	Eco.	94 Apr	96 Mar	30.9	30.5	15.0	14.8	-	-	-	-
			96 Apr	03 Mar	22.0	24.7	11.4	12.7	1.12	67	-0.17	67
Nonodake	Pacific ocean	Rural	88 Apr	94 Mar	9.5	12.8	9.4	12.6	-0.12	60	-0.08	60
			94 Apr	03 Mar	12.3	15.5	12.0	14.8	0.63	97	0.26	97
Sendai	Pacific ocean	Urban	88 Apr	03 Mar	20.1	22.4	16.2	18.2	-0.47	154	-0.21	154
Oze	Pacific ocean	Eco.	95 Apr	03 Mar	Invalid data for no or less data in winter.							
Nikkou	Pacific ocean	Eco.	97 Apr	03 Mar	Invalid data for no or less data in winter.							
Akagi	Pacific ocean	Eco.	96 Apr	03 Mar	Invalid data for no or less data in winter.							

Tsukuba	Pacific ocean	Rural	88	Apr	–	94	Mar	21.5	19.2	17.8	16.2	–1.17	61	–0.09	61	–0.72	61	0.12	61
			94	Apr	–	03	Mar	17.0	24.0	13.9	19.7	0.53	99	–0.72	99	0.39	99	–1.36	99
Kashima	Pacific ocean	Urban	88	Apr	–	00	Mar	31.4	17.1	22.9	12.8	–1.04	131	0.22	127	–0.46	131	0.69	131
			00	Apr	–	03	Mar	–	–	–	–	–	–	–	–	–	–	–	–
Tokyo	Pacific ocean	Urban	88	Apr	–	00	Mar	Invalid data due to contamination from a neighboring tree.											
			88	Apr	–	03	Mar	18.1	17.1	14.3	13.6	–0.32	162	–0.21	161	–0.10	162	–0.07	162
Ichihara	Pacific ocean	Urban	88	Apr	–	03	Mar	27.1	23.2	17.9	15.8	–0.61	158	0.06	157	–0.05	158	0.37	158
Kawasaki	Pacific ocean	Urban	88	Apr	–	03	Mar	19.3	26.4	7.8	11.2	0.35	88	0.02	88	0.09	88	–0.09	88
Tanzawa	Pacific ocean	Eco.	95	Apr	–	03	Mar	26.4	7.8										
Inuyama	Pacific ocean	Rural	88	Apr	–	00	Mar	19.2	26.7	12.6	17.4	–0.30	137	0.16	137	–0.26	137	0.21	137
			00	Apr	–	03	Mar	29.1	34.1	21.2	25.0	–	–	–	–	–	–	–	–
Nagoya	Pacific ocean	Urban	88	Apr	–	03	Mar	20.6	25.3	14.8	18.3	–0.45	159	–0.33	159	–0.24	159	–0.02	159
			94	Apr	–	99	Mar	20.5	25.5	11.5	14.3	0.06	55	0.18	56	–0.04	55	0.00	56
Utsio-cape	Pacific ocean	Remote	99	Apr	–	03	Mar	21.6	22.3	8.8	9.2	–	–	–	–	–	–	–	–
			94	Apr	–	00	Mar	31.9	31.6	11.5	11.5	0.42	58	0.38	60	–0.04	58	0.05	60
Ashizuri-cape	Pacific ocean	Remote	92	Apr	–	99	Mar	13.3	6.2	8.6	4.4	0.63	77	0.05	76	0.18	82	0.03	83
			99	Apr	–	03	Mar	7.6	4.9	4.2	2.9	–	–	–	–	–	–	–	–
Kyoto-Yawata	Inland sea	Rural	88	Apr	–	00	Mar	Invalid data due to contamination from a neighboring tree.											
			00	Apr	–	03	Mar	–	–	–	–	–	–	–	–	–	–	–	–
Amagasaki	Inland sea	Urban	88	Apr	–	03	Mar	15.5	15.4	14.5	14.6	–0.67	159	–0.19	159	–0.65	159	–0.19	159
			88	Apr	–	00	Mar	19.1	16.8	15.4	14.1	–0.67	97	0.49	97	–0.38	97	0.72	97
Osaka	Inland sea	Urban	00	Apr	–	03	Mar	16.8	17.8	14.3	15.0	–	–	–	–	–	–	–	–
			88	Apr	–	03	Mar	14.6	14.9	15.1	15.8	–0.41	164	–0.13	164	–0.15	164	0.20	164
Kurashiki	Inland sea	Rural	88	Apr	–	00	Mar	24.0	20.3	17.6	14.9	–0.79	128	0.33	128	–0.91	128	0.16	128
			00	Apr	–	03	Mar	24.9	28.3	19.1	21.6	–	–	–	–	–	–	–	–
Ube	Inland sea	Urban	88	Apr	–	03	Mar	33.5	22.3	23.5	15.9	–1.16	169	–0.45	169	–0.85	169	–0.24	169
			94	Apr	–	03	Mar	20.7	13.4	12.7	8.2	–0.01	96	0.05	96	–0.11	96	–0.06	96
Oita-Kujiyu	Inland sea	Eco.	91	Apr	–	03	Mar	32.6	30.5	16.2	15.1	0.10	118	0.43	118	0.02	118	0.29	118
			88	Apr	–	00	Mar	39.3	38.1	26.1	25.4	–0.74	138	0.79	139	–0.31	138	0.84	139
Kitakyushu	East China sea	Urban	88	Apr	–	03	Mar	27.4	19.1	17.3	11.6	0.12	175	0.67	175	–0.06	175	0.48	175
			88	Apr	–	03	Mar	34.1	19.0	20.5	11.6	–1.12	164	–0.10	164	–1.17	164	–0.27	164
Omuta	East China sea	Urban	88	Apr	–	03	Mar	18.5	17.3	12.8	12.0	0.12	96	0.12	96	0.01	96	0.00	96
			94	Apr	–	03	Mar	37.0	32.5	12.6	11.0	0.19	94	0.42	94	0.03	94	0.11	94
Goto	East China sea	Remote	94	Apr	–	03	Mar	37.0	32.5	12.6	11.0	0.19	94	0.42	94	0.03	94	0.11	94
			94	Apr	–	03	Mar	37.0	32.5	12.6	11.0	0.19	94	0.42	94	0.03	94	0.11	94
Yakushima	Southwest Island	Eco.	94	Apr	–	03	Mar	37.0	32.5	12.6	11.0	0.19	94	0.42	94	0.03	94	0.11	94
			92	Apr	–	01	Mar	21.4	20.0	8.7	8.1	0.33	94	0.26	96	0.01	94	0.00	96
Amami	Southwest Island	Remote	01	Apr	–	03	Mar	21.4	20.0	8.7	8.1	0.33	94	0.26	96	0.01	94	0.00	96
			01	Apr	–	03	Mar	20.1	18.2	8.6	7.8	–	–	–	–	–	–	–	–
Okinawa-Kunigami	Southwest Island	Remote	94	Apr	–	00	Mar	19.8	17.7	7.2	6.4	0.29	61	0.31	62	0.03	61	0.07	62
			94	Apr	–	00	Mar	19.8	17.7	7.2	6.4	0.29	61	0.31	62	0.03	61	0.07	62

$p < 0.05$

“–” no annual means or annual change rates were not evaluated because of the Japan's data completeness criteria (Ministry of the Environment 2004)

Table 2 Annual medians and standard deviations for precipitation amounts and depositions of nss-sulfate and nitrate in Japan

Fiscal year	Annual precipitation amounts			Annual Depositions					
				nss-SO ₄ ²⁻			NO ₃ ⁻		
	n	Median	Standard deviation	n	Median	Standard deviation	n	Median	Standard deviation
		mm			mmol m ⁻²			mmol m ⁻²	
1988	10	1385.0	316.3	9	26.4	11.2	9	18.3	5.8
1989	19	1427.5	241.1	18	27.0	9.4	18	18.5	6.2
1990	19	1483.0	293.1	18	24.9	10.8	18	22.2	7.3
1991	23	1549.0	430.4	22	27.7	12.9	22	21.7	8.9
1992	22	1193.8	280.5	21	19.5	10.3	21	13.8	9.1
1993	23	1605.0	513.2	22	20.1	11.3	22	19.3	9.0
1994	31	985.0	392.5	31	14.9	7.1	31	15.6	6.7
1995	38	1540.9	496.5	38	23.0	9.7	38	21.6	9.2
1996	39	1254.0	427.2	39	18.3	8.2	39	22.9	9.3
1997	40	1858.2	617.3	40	20.7	8.0	40	24.5	7.9
1998	42	1699.7	835.2	38	19.3	8.6	38	23.5	9.9
1999	39	1752.0	698.7	31	18.3	8.4	31	21.3	8.6
2000*	45	1517.2	671.7	38	26.3	11.0	39	20.0	10.9
2001	44	1523.2	621.5	40	22.5	9.2	40	21.4	9.4
2002	43	1435.1	726.1	32	22.2	9.1	33	21.1	10.9

*In 2000, Mt. Oyama started its volcanic eruption

the volcano have decreased. However, this inventory does not include the volcanic emissions from Mt. Oyama on Miyakejima Island, which started to erupt suddenly and violently in 2000. In this study, Mt. Oyama on Miyakejima Island is not included as a volcano.

Inventories of anthropogenic SO₂ and NO₂ emissions in Japan, China, and South Korea were obtained from reports noted in the references (Akimoto and Narita 1994; Cha and Seok 1999; Ichikawa and Fujita 1995; Ikeda and Higashino 1997; Kannari et al. 2003; Park and Kim 1997; Shen and Zhao 1992; Shusheng 1999; State Environmental Protection Administration of China 2002; Streets and Waldhoof 2000; Tonooka 1999; Wang et al. 1992). Emission inventories were not evaluated in this study but cited from reliable scientific publications. The number and kinds of emission sources discussed in each reference paper were different from paper to paper. The common anthropogenic sources among them were industry, energy, incineration, and transportation. Emissions data taken from the cited references have in some cases been averaged to annual mean values. For the trends of anthropogenic emissions, annual change rates were calculated based on the annual

mean values of SO₂ and NO₂ emissions by the least squares model.

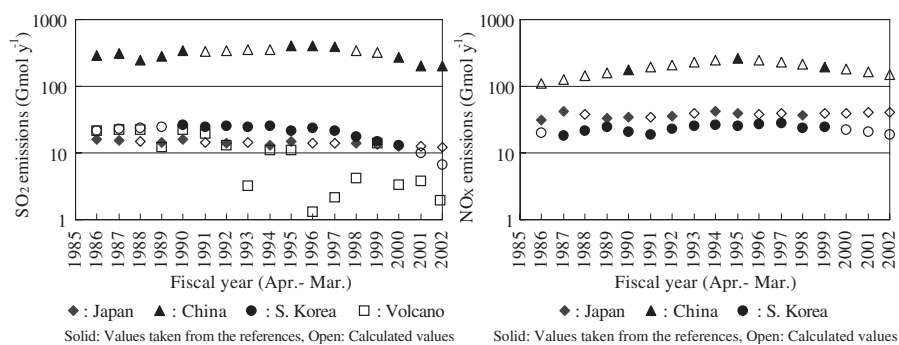
Concerning anthropogenic SO₂ emissions, those in Japan have decreased slightly due to the desulfurization of light oil, as shown in Fig. 2 (MOE 2004). Furthermore, emissions in South Korea have also decreased slightly. Those in China were stable until 1997 and decreased after that.

Anthropogenic NO₂ emissions in Japan and South Korea have increased slightly, as shown in Fig. 2. On the other hand, emissions in China increased from 1995 through 1999 and decreased after that.

Relative to emissions, the decline in the volcanic SO₂ emissions was remarkable.

3.2 Quantitative Discussions for Wet Depositions of nss – SO₄²⁻ and NO₃⁻

Ikeda and Higashino (1997) reported that the simulated concentrations of SO₄²⁻ and NO₃⁻ in precipitation indicate a reasonable agreement with the observed values from 16 sites in Japan. The contributions of anthropogenic emissions in Japan, China, and South Korea and the volcanic emissions in Japan to

Fig. 2 SO₂ and NO_x emissions in Japan, China, and Korea

deposition of SO₄²⁻ and NO₃⁻ in precipitation in 1990 were reported as shown in Table 3.

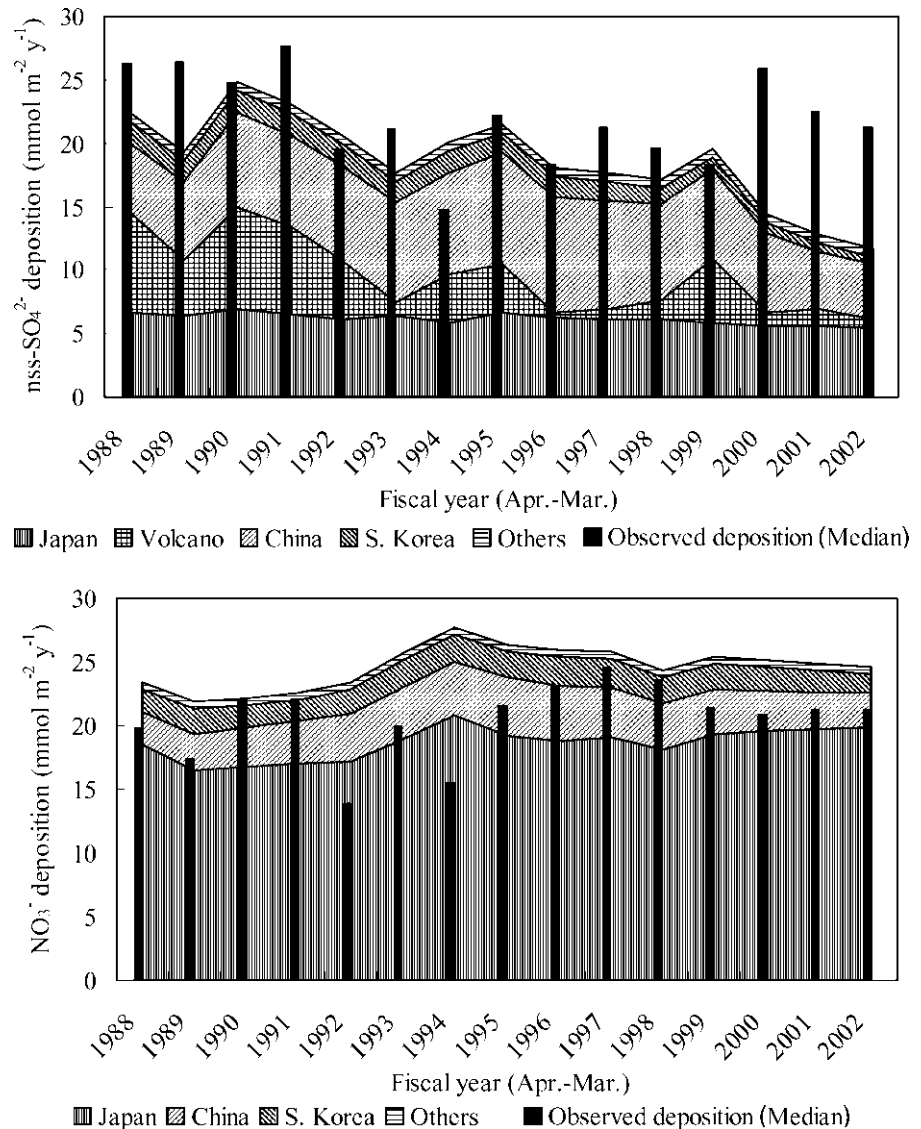
Our quantitative analysis was based on the relative contributions for 1990, designated as the initial condition, reported by Ikeda and Higashino (1997). In the initial condition, observational median depositions were matched with the calculated contribution of emissions to precipitation components and the intensity of each emission in 1990, as shown in Fig. 3. The

contribution of emissions and the estimated depositions from other years were calculated by the intensity of each emission for each year. In addition, the other emissions, which Ikeda and Higashino (1997) concluded to account for some 3% of the total deposition, did not significantly affect Japan's precipitation chemistry. Therefore, the other emissions from Japan, China, and South Korea were assumed to be invariant during the period of interest.

Table 3 Contributing emission sources of calculated nss-sulfate and nitrate deposition in Japan

	Fiscal year	Anthropogenic emissions			Volcano	Others
		Japan	China	S.Korea	Japan	
		%	%	%	%	%
Sulfate	1990	28	30	7	32	3
	1991	28	31	7	30	3
	1992	30	37	8	22	3
	1993	36	44	10	6	4
	1994	29	40	9	19	3
	1995	31	41	7	18	3
	1996	34	50	9	3	4
	1997	35	49	8	4	4
	1998	36	44	7	9	4
	1999	30	36	5	26	3
	2000	38	42	6	8	5
	2001	44	35	5	11	5
Nitrate	2002	46	38	4	6	6
	1990	76	14	8	—	2
	1991	75	15	7	—	2
	1992	74	16	8	—	2
	1993	74	16	8	—	2
	1994	75	15	8	—	2
	1995	73	17	8	—	2
	1996	73	17	9	—	2
	1997	74	16	9	—	2
	1998	74	15	8	—	2
	1999	76	14	8	—	2
	2000	78	13	7	—	2
	2001	79	12	7	—	2
	2002	81	11	6	—	2

Fig. 3 Deposition of $\text{nss} - \text{SO}_4^{2-}$ and NO_3^- and the contribution of precursor emissions



According to our calculations, the variation in the calculated depositions of $\text{nss} - \text{SO}_4^{2-}$ in precipitation and the median values from the observations are shown to have similar intensity and trends in the observed medial values from *FY* 1988 to *FY* 1998

(Fig. 3). However, the calculated depositions of $\text{nss} - \text{SO}_4^{2-}$ were underestimated after *FY* 2000 because these model inventories did not include the SO_2 emissions from Mt. Oyama on Miyakejima Island, which started to erupt in *FY* 2000. The contributing

Table 4 Contributing emission sources of observed nss-sulfate deposition in Japan when the excess amounts of observed depositions after *FY* 2000 were estimated as effects from Mt.Oyama

	Fiscal Year	Anthropogenic emissions			Volcano	Others	Mt. Oyama
		Japan	China	S. Korea			
		%	%	%	%	%	%
Sulfate	2000	21	24	3	5	3	44
	2001	25	20	3	6	3	43
	2002	25	21	2	3	3	46

values of anthropogenic emissions in Japan and China have increased, and those from volcanoes in Japan have decreased (Table 3). Moreover, the contributing values of anthropogenic emissions in Japan, China, and South Korea and the emissions from Mt. Oyama and other volcanoes in Japan were calculated as shown in Table 4, when the excess amounts of observed depositions after FY 2000 were estimated as effects from Mt. Oyama. However, these contributing values will change rapidly because the SO₂ emissions from Mt. Oyama are decreasing after FY 2002.

For NO₃⁻, both the calculated and observed depositions were slightly increasing; however, the calculation exceeded the observation. More investigation will be required to determine the effects of the chemical reaction because the annual mean of the O₃ concentration in the base year, FY 1990, was higher than that in other years.

Calori et al. (2001) reported that the calculated nss – SO₄²⁻ depositions increased during 1985–1997. Their contributing factors of the sources to the sulfur emissions were similar to those we employed. The anthropogenic emissions in China, however, were not increased as projected in their work. Volcanic sulfur dioxide emissions fluctuated more than estimated. These conflicting results were, therefore, attributable to the unexpected changes in the actual emissions.

4 Conclusion

Based on the results of the analysis of the relationships between the precursor emissions and depositions of nss – SO₄²⁻ and NO₃⁻ of the JADS from FY 1988 to FY 2002, the following conclusions were drawn:

- (1) For nss – SO₄²⁻, the calculated deposition agrees well with the intensity and trends up to FY 1999. The decline of depositions seemed to be caused mainly by the decreasing trend of SO₂ emissions from volcanoes.
- (2) After FY 2000, a higher nss – SO₄²⁻ deposition than had been projected in preceding years was evident, which is attributable to the volcanic SO₂ from Mt. Oyama on Miyakejima Island. Except for the effects of this eruption, the contribution of anthropogenic emissions in China or Japan was the largest.

- (3) For NO₃⁻, both the calculated and observed depositions showed a slight increase although the calculation was found to exceed the observation. More investigation will be required to thoroughly understand the details of the chemical reaction.

References

- Akimoto, H., & Narita, H. (1994). *Atmospheric Environment*, 28, 213–225.
- Calori, G., Carmichael, G. R., Street, D., Thongboonchoo, N., & Guttikunda, S. K. (2001). *Journal of Global Environmental Engineering*, 7, 1–16.
- Cha, J., & Seok, K. (1999). *Proceedings of Expert Group Meeting on Emission Monitoring and Estimation, Niigata, Japan*.
- Fujita, S., Tonooka, Y., & Ohta, K. (1992). *Journal of Japan Society for Atmosphere Environment*, 27, 336–343 (in Japanese).
- Hayashi, K., Noguchi, I., Ohizumi, T., Aikawa, M., Kitamura, M., Takahashi, A., et al. (2006). *IGACTivities*, 33, 2–6.
- Hayashi, K., Noguchi, I., Ohizumi, T., Aikawa, M., Takahashi, A., Tanimoto, H., et al. (2005). *3rd International Nitrogen Conference Contributed Papers* (598–608). USA: Science Press.
- Ichikawa, Y., & Fujita, S. (1995). *Water, Air, and Soil Pollution*, 85, 1927–1932.
- Ikeda, Y., & Higashino, H. (1997). *Journal of Japan Society for Atmosphere Environment*, 32, 175–186 (in Japanese).
- Kannari, A., Tonooka, Y., & Murano, K. (2003). *Environmental Research Quarterly*, 129, 35–46 (in Japanese).
- Ministry of the Environment (2004). *Comprehensive Summary Report on Acid Deposition Monitoring Survey*, 8–93 (in Japanese).
- Park, S. U., & Kim, C. H. (1997). *Proceedings of the International Workshop on Unification of Monitoring Protocol of Acid Deposition and Standardization of Emission Inventory*, 98–123.
- Seto, S., Nakamura, A., Noguchi, I., Ohizumi, T., Fukuzaki, N., Toyama, S., et al. (2002). *Atmospheric Environment*, 36, 3505–3517.
- Shen, D., & Zhao, D. (1992). *International Symposium on Emissions Inventory and Prevention Technology for the Atmospheric Environment, Tsukuba, Japan*, 92–102.
- Shusheng, L. (1999). *Proceedings of Expert Group Meeting on Emission Monitoring and Estimation, Niigata, Japan*.
- State Environmental Protection Administration of China (2002). Web site, <http://www.zhb.gov.cn/>.
- Streets, D. G., & Waldhoff, S. T. (2000). *Atmospheric Environment*, 34, 363–374.
- Takahashi, A., & Fujita, S. (2000). *Atmospheric Environment*, 34, 4551–4555.
- Tonooka, Y. (1999). *Proceedings of Expert Group Meeting on Emission Monitoring and Estimation, Niigata, Japan*.
- Wang, W., Shi, Q., & Shu, Y. (1992). *International Symposium on Emissions Inventory and Prevention Technology for the Atmospheric Environment, Tsukuba, Japan*, 43–53.

Sulphate and Nitrate in Precipitation and Soil Water in Pine Forests in Latvia

E. Terauda · O. Nikodemus

Received: 12 June 2005 / Accepted: 23 June 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract The $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ concentrations and pH in bulk precipitation, throughfall, stemflow and soil water for the 1994–2004 period were studied in pine forests in Latvia (Rucava and Taurene Integrated Monitoring stations). The $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ concentrations decreased over the study period, simultaneously with a decrease of acidity in precipitation. The changes were more evident in the western part of Latvia, probably due to declining long-range air pollution from West Europe. The trend of decreasing sulphate concentrations and increasing pH in precipitation were not followed by respective changes in soil water. In the upper soil horizon sulphate ion concentrations and acidity increased in soil water. Over the observation period, nitrate concentrations also showed an increasing trend in soil water at Rucava and Taurene, but these changes were not statistically significant.

Keywords bulk precipitation · nitrate · pine forest · soil water · stemflow · sulphate · throughfall

1 Introduction

Many environmental pollutants (particularly S and N compounds) can affect functioning of forest ecosys-

tems (Luttermann & Freedman, 2000). The availability of N compounds controls many aspects of biogeochemical processes and exerts a strong influence on net primary production in terrestrial ecosystems (Schachtschabel, Blume, Brümmer, Hartge, & Schwertmann, 1989). Deposition of N and S can cause soil acidification, leading to leaching of base cations and aluminium from the soil (Stoddard et al., 1999) and increased movement of nitrogen compounds and base cations into surface waters (Beier, Eckersten, & Gundersen, 2001). It has been proposed that more forest ecosystems will reach the stage of nitrogen saturation and that nitrogen leaching from soil may increase (Eichhorn, Haussmann, Paar, Reinds, & Vries, 2001).

Forest canopies capture aerosol – gaseous forms of elements, supplementing the element pool received by the ecosystems from the atmosphere (Bytnerowicz & Fen, 1996; Lee, Dollard, Derwent, & Pepler, 1999). Tree canopies can absorb nitrogen from the atmosphere, and this process relates to both ammonium and nitrate ions (Stachurski & Zimka, 2000). Considerable changes occur in element concentrations as precipitation water passes through tree canopies. Concentrations of chemical substances in bulk precipitation, throughfall and stemflow differ disparately (Ukonmaanaho, 2001).

Up to now, studies on the concentrations and deposition of pollutants from the atmosphere and their possible impact on the forest ecosystems in Latvia have relied mainly on data regarding the chemical composition

E. Terauda (✉) · O. Nikodemus
Faculty of Geography and Earth Sciences,
University of Latvia, 19 Rainis Blvd., Riga 1586, Latvia
e-mail: evija.terauda@lu.lv

of bulk precipitation (Laivins, Lulko, & Frolova, 1996). More recently, investigations of quantitative and qualitative indices of water flow in forest ecosystems in Latvia can provide new information about pollutant transformations in the forest canopy and soil buffer capacity, and chemical element outputs from forest soil. This is especially important for forests in the boreo-nemoral zone, where these types of studies are few. In this paper, we present data on $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ concentrations in bulk precipitation as it passes through the canopy and soil humus layer of a coniferous stand. The objectives of the study were: (1) to present the changes and time trends of $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ concentrations and pH in bulk precipitation (BP), throughfall (TF), stemflow (SF) and soil water (SW) at two ICP-IM stations in Latvia during the period 1994–2004; (2) to evaluate differences between the concentrations in BP, TF, SF and SW; (3) to assess relationships between sulphate and nitrate concentrations in SW and precipitations.

2 Materials and Methods

For this study, data from the Integrated Monitoring (IM) network were used, which in Latvia includes the Latvian Environment, Geology and Meteorology Agency in cooperation with the University of Latvia.

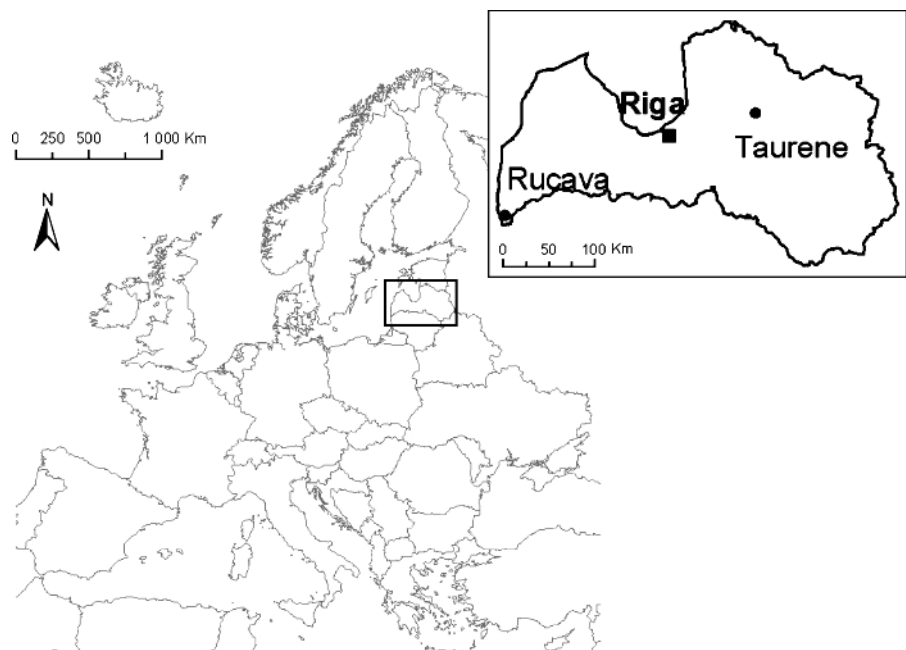
2.1 Study Area

Two Integrated Monitoring (IM) stations, in Rucava and Taurene, have been established in Latvia. These stations are located in two different natural regions: the Coastal Lowland and central part of Latvia on the Vidzeme Upland (Fig. 1). Each station is situated in forested and undisturbed areas. The dominant tree species in the Rucava stand is Scots pine (*Pinus sylvestris*). The Taurene stand is a mixture of Scots pine, Norway spruce (*Picea abies*), and birch (*Betula pendula*). The canopy coverage in the Rucava stand is 85% but in the Taurene stand 70%. The soil type at both locations is Haplic podzol on sand parental soil.

2.2 Sample Collection and Analysis

The sampling procedures and methods followed the standards of the Integrated Monitoring Manual (Manual for Integrated Monitoring, 1998). Three bulk precipitation (BP) collectors (NILU type) were placed in an open area at a height of 120 cm and such that the nearest trees did not shadow the collectors. They remained open constantly, even when there was no precipitation. During winter, buckets were used for snow sampling. Throughfall (TF) was collected with seven funnel-type collectors in summer and with

Fig. 1 Location of the study sites



buckets in winter. The BP and TF collection bottles were covered with aluminium foil to keep the samples cool and dark. Stemflow (SF) water was collected at each IM station from the dominant species – Scots pine. Spiral type collectors were installed around 10 trees per site. The BP was collected once every 10 days, TF and SF were collected every 15 days. Collection of SF was performed only during the snow-free period. The samples were composited once a month for an average sample.

Soil water (SW) was collected using two humus (cylinder) type lysimeters, which were installed at a 10-cm depth to collect water, filtered through the O horizon. The soil water was pumped out at the end of each month, but in spring immediately after soil thaw.

Chemical analyses were performed for pooled monthly samples. The samples were stored in dark and cool (+4°C) conditions until analysis. Before analysis TF and SF samples were filtered using Schleicher & Schuell 589² filter paper. The pH was determined by potentiometric method immediately after sampling and the SO₄-S and NO₃-N levels by ion chromatography (Manual for Integrated Monitoring, 1998).

2.3 Data Handling and Statistical Analysis

Annual precipitation-weighted mean concentrations were calculated for each site. Annual deposition values were calculated by multiplying the concentration from collected samples by the corresponding amount of precipitation (in mm).

The pH values were converted to H⁺ before calculation of the mean pH value. Because of a non-normal distribution, non-parametric statistics were used: Mann–Kendall test for detecting trends in the time series, Paired-Samples *T*-test for testing differences between mean annual concentrations in BD, TF, SF and SW, Mann–Whitney *U* test for testing differences between IM plots. A significance level of $p < 0.05$ has been chosen to represent a statistically significant difference between data sets.

3 Results and Discussion

The amount of precipitation during the study period varied from 395.5 to 973.8 mm at Rucava, and from 470.6 to 801.3 mm at Taurene (Table 1). Sulphate and nitrate in the atmosphere can have significant impact on the pH of precipitation. The mean annual pH of BP within the study period varied from 4.5 (± 0.89) in 1996 to 5.9 (± 0.79) in 2004 at Rucava IM site and from 4.8 (± 1.02) in 1997 to 5.8 (± 0.66) in 2002 at Taurene IM site. Although there is no explicit tendency growth of precipitation pH per years, the positive linear trend for pH was statistically significant ($p < 0.05$) at both stations during 1994–2004 (Fig. 2). Similarly, pH significantly increased also in TF. The mean annual pH of TF at Rucava increased from 4.4 (± 0.42) to 5.4 (± 0.81), but at Taurene from 4.5 (± 0.5) to 5.8 (± 0.67). The mean annual pH in SF at both monitoring stations was significantly lower than in BP and TF (Fig. 3). Throughfall and stemflow of coniferous forests usually have a lower pH than bulk precipitation. This represents an increase in free acidity under coniferous canopy. Therefore, acid interception by the conifer canopy is higher than dry deposited basic compounds or buffering capacity (Pajuste, 2004). As the water flows through the canopy and along the stem, it absorbs solutes and dry deposition captured by the surface of the needles and bark (Parker, 1983). Stemflow average pH parameters in Rucava per years varied from 3.9 (± 0.19) to 4.2 (± 0.27), but in Taurene from 3.8 (± 0.1) to 4.4 (± 0.72).

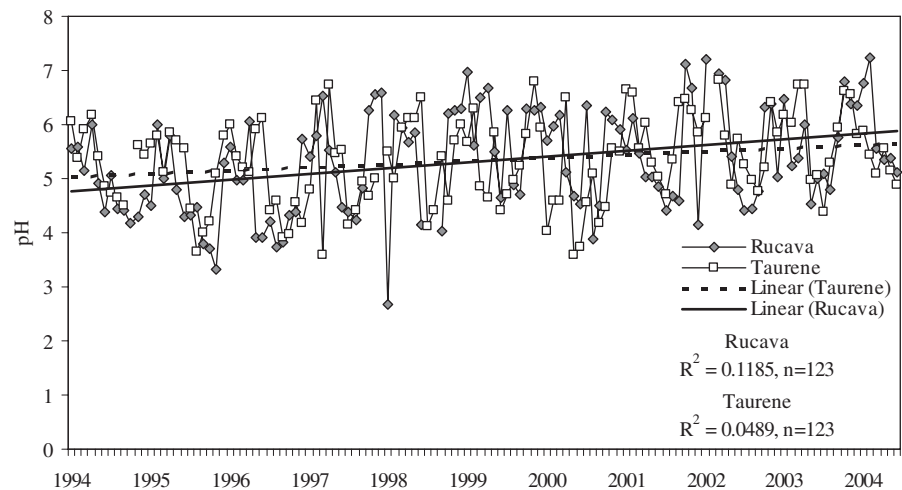
The increase of precipitation pH value in recent years in BP and TF has been explained by a greater decrease in acidic anion concentrations (Moffat, Kvaalen, Solberg, & Clarke, 2002).

At IM stations in Latvia the SO₄-S ion concentrations in both BP and TF and SF showed a significant negative linear trend (Fig. 4). The weighted annual mean SO₄-S ion concentrations in BP at Rucava changed from 2.54 (± 1.38) in 1997 to 0.52

Table 1 The annual precipitation (mm) amount at the Rucava (R IM) and Taurene (T IM) Integrated Monitoring stations 1994–2004

	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
R IM	490.5	631.5	395.5	468.7	973.8	527.7	639.9	846.1	765.3	794.6	586.2
T IM	518.0	666.3	480.4	506.5	727.9	470.6	756.0	693.8	644.2	716.3	801.3

Fig. 2 pH changes in bulk precipitation at the Rucava and Taurene IM stations



(± 0.28) mg/l in 2000, in TF from 4.43 (± 2.39) in 1997 to 0.89 (± 0.56) mg/l in 2000 and in SF from 9.79 (± 3.56) in 1997 to 2.45 (± 1.14) mg/l in 1998, but at Taurene, respectively, from 1.84 (± 1.4) in 1997 to 0.4 (± 0.12) mg/l in 2004, from 2.47 (± 1.76) in 1997 to 0.56 (± 0.22) mg/l in 2004 and from 6.95 (± 2.17) in 1995 to 0.98 (± 0.61) mg/l in 2002. More significant decrease in $\text{SO}_4\text{-S}$ concentrations and acid precipitation were observed in Rucava compared to Taurene and this could be related to a declining impact of long-range transboundary air pollution in Latvia.

The concentrations of $\text{SO}_4\text{-S}$ in Taurene and Rucava increased in the order: $\text{BP} < \text{TF} < \text{SF}$. Sulphate concentrations in TF and SF were significantly higher than those in BP (Table 2).

Because SO_4^{2-} shows little interaction with canopies (Bredemeier, 1988; Lindberg, Lovett, Richter, & Johnson, 1986), the SO_4^{2-} enrichment of throughfall and stemflow is primarily the result of wash-off of

accumulated dry deposition (Lindberg & Lovett, 1992). The very high sulphate concentration in BP, TF and SF at Rucava and Taurene in 1997 was related with a relatively dry year in 1996 (Table 1) and increased dry element deposition and accumulation on pine needles, branches and stems.

The mean annual deposition of $\text{SO}_4\text{-S}$ through BP and TF is presented in Table 3. Stemflow, particularly in coniferous forests, has little importance on contribution to ion fluxes at the stand scale but is important at the scale of individual trees (Gower, Rowell, Nortcliff, & Wild, 1995; Ukonmaanaho, 2001). The SF volumes were very small, representing only 0.3% in Rucava and 0.4% in Taurene of the rainfall, and therefore it is not considered further in deposition calculations. Although greater $\text{SO}_4\text{-S}$ deposition through BP and TF were observed in Rucava compared to Taurene, the observed changes between the IM stations were not statistically significant and the differences between BP and TF were not substantial.

The deposition of $\text{SO}_4\text{-S}$ derived from BP and TF did not change during the monitoring period. The only statistically significant decreasing trend was estimated for $\text{SO}_4\text{-S}$ deposition in BP at Taurene, where the annual mean $\text{SO}_4\text{-S}$ of precipitation dropped from 9.32 to 3.2 $\text{kg/ha}^{-1}/\text{yr}^{-1}$. The highest deposition of $\text{SO}_4\text{-S}$ through BP in IM stations 10.61 (± 1.82) $\text{kg/ha}^{-1}/\text{yr}^{-1}$ was observed in 1997, but the lowest 3.4 (± 0.3) $\text{kg/ha}^{-1}/\text{yr}^{-1}$ in 2004. The respective values through TF were 15.91 (± 8.1) $\text{kg/ha}^{-1}/\text{yr}^{-1}$ in 1997 and 4.5 (± 1.03) $\text{kg/ha}^{-1}/\text{yr}^{-1}$ in 2004.

During our observation period, the concentrations of nitrate ions in precipitation both in Rucava and in

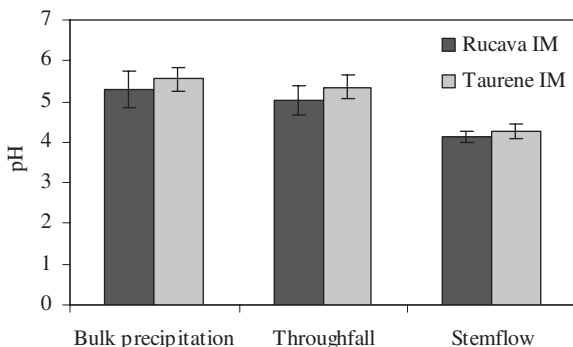
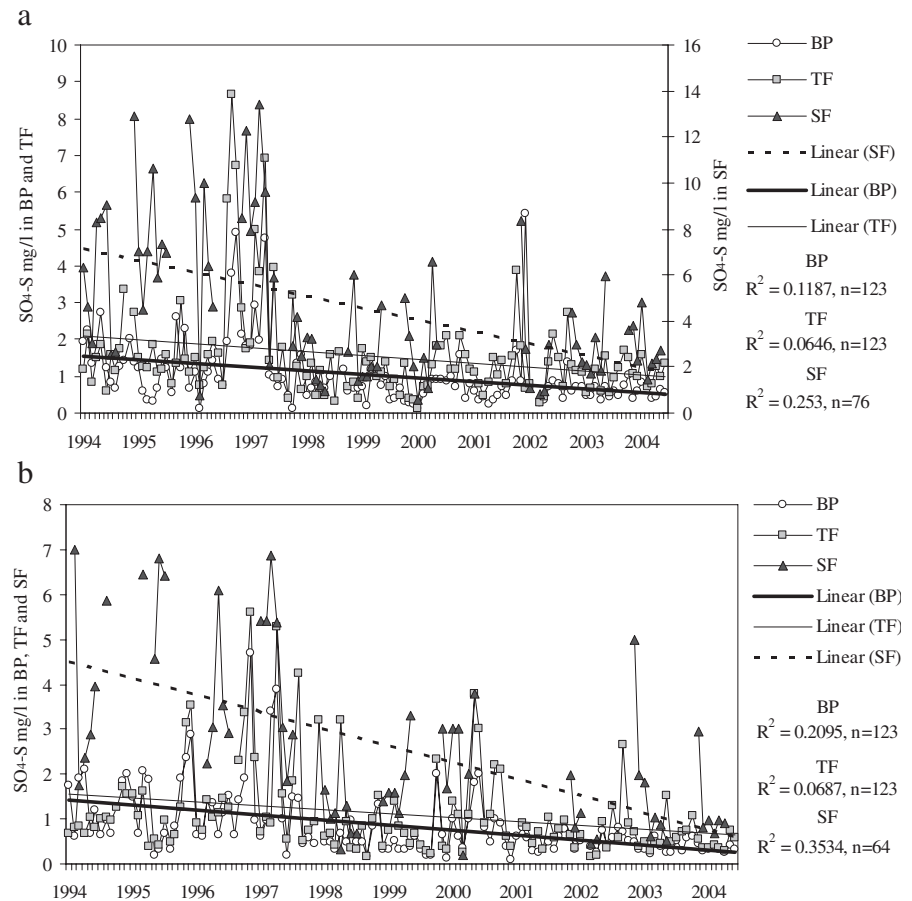


Fig. 3 Annual mean pH ($\pm$ standard deviation) of bulk precipitation, throughfall and stemflow at the Rucava and Taurene IM stations during 1994–2004

Fig. 4 $\text{SO}_4\text{-S}$ concentrations in bulk precipitation (BP), throughfall (TF) and stemflow (SF) at the Rucava (a) and Taurene (b) IM stations



Taurene IM stations showed decreasing trends (Fig. 5). However, compared to changes in $\text{SO}_4\text{-S}$ concentration, where the decrease was statistically significant, the decline in $\text{NO}_3\text{-N}$ in neither studied types of precipitation was considerable, except in stemflow at Rucava.

Nitrate concentrations in TF and SF were significantly higher than in BP at Rucava station but the differences at Taurene station were not statistically significant (Table 2). Results showed that in boreo-nemoral forests in Latvia the mean concentrations of $\text{NO}_3\text{-N}$ in water

Table 2 Mean (volume-weighted) annual concentration ($\pm$ standard deviation) from monthly data in bulk precipitation (BP), throughfall (TF), stemflow (SF) and soil water (SW) under O horizon during 1994–2004

	$\text{SO}_4\text{-S}$ (mg/l)		$\text{NO}_3\text{-N}$ (mg/l)	
Rucava				
BP	1.00 ± 0.56	a	0.67 ± 0.22	b
TF	1.55 ± 0.98	b	0.87 ± 0.17	c
SF	4.63 ± 2.44	c	3.87 ± 3.19	d
SW	5.54 ± 1.35	cd	0.07 ± 0.05	a
Taurene				
BP	0.84 ± 0.47	a	0.45 ± 0.13	b
TF	1.12 ± 0.54	b	0.56 ± 0.19	bc
SF	3.07 ± 2.16	c	0.76 ± 0.76	bcd
SW	5.04 ± 1.8	cd	0.04 ± 0.02	a

For each ion values followed by the same letter do not significantly ($p < 0.05$) differ from each other

Table 3 Comparison between mean ($\pm$ standard deviation) deposition of ions through bulk precipitation (BP) and throughfall (TF) for the Rucava and Taurene IM stations during 1994–2004

	Rucava IM	Taurene IM	<i>U</i> test
SO ₄ -S (kg/ha ⁻¹ year ⁻¹)			
BP	6.33 $\pm$ 2.57	5.07 $\pm$ 2.21	n.s
TF	7.93 $\pm$ 4.86	5.73 $\pm$ 2.2	n.s
NO ₃ -N (kg/ha ⁻¹ year ⁻¹)			
BP	4.41 $\pm$ 1.65	2.21 $\pm$ 0.92	*
TF	4.38 $\pm$ 1.08	2.91 $\pm$ 1.1	*

*= p <0.05; n.s.=not significant

types did not follow the order BP>TF>SF as it was found in other studies. Such a pattern is typical in boreal forest ecosystems and is explained by a shortage of available nitrogen (Ukonmaanaho, 2001). The deposition fluxes of nitrate were significantly greater

in Rucava compared to Taurene (Table 3) but the differences between BP and TF were not statistically significant.

Precipitation intensity and chemical composition impact soil water chemical composition collected

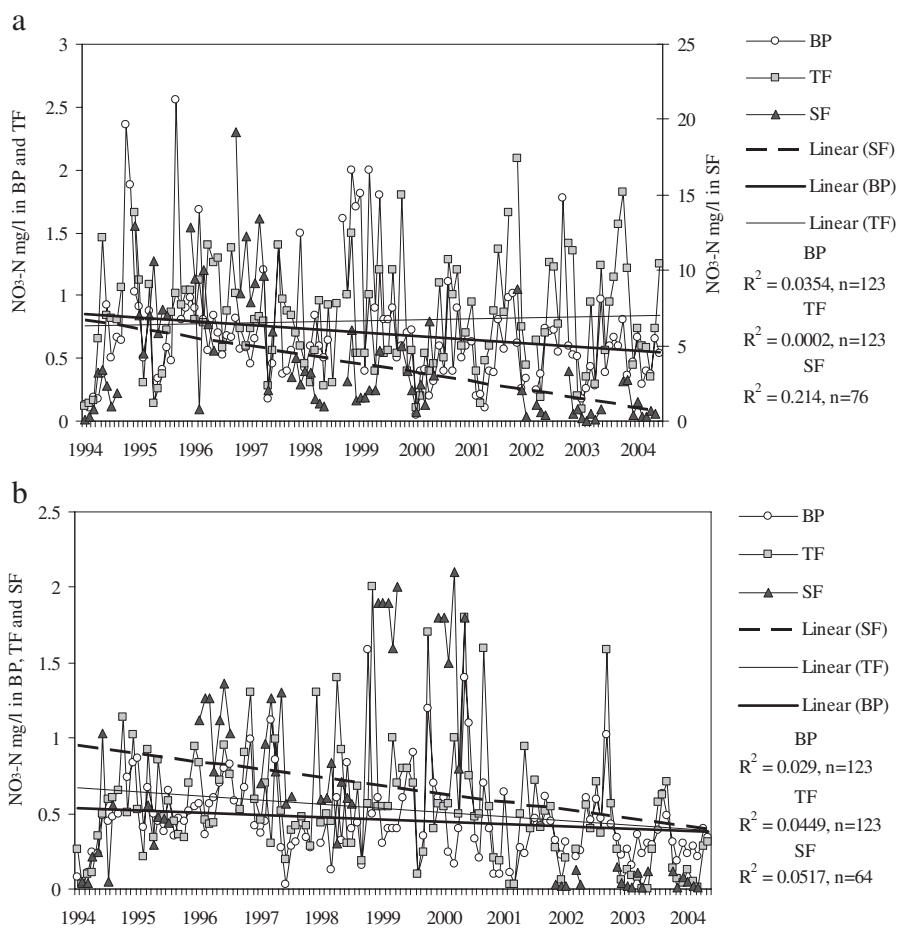
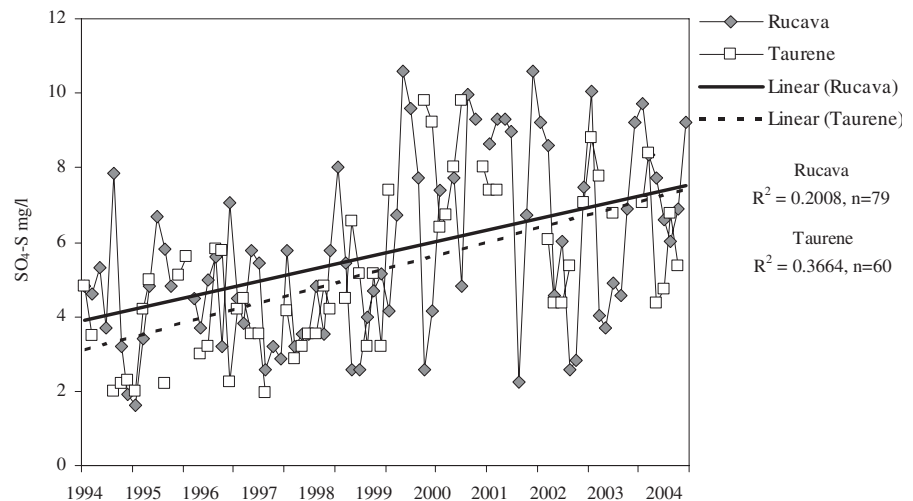
Fig. 5 NO₃-N concentrations in bulk precipitation (BP), throughfall (TF) and stemflow (SF) at the Rucava (a) and Taurene (b) IM stations

Fig. 6 $\text{SO}_4\text{-S}$ concentrations in soil water in upper soil horizon (10-cm) at the Rucava and Taurene IM stations



below the soil organic layer (10 cm depth), which reacts most quickly to changes in precipitation chemical composition.

The annual mean pH values of SW did not change significantly at Rucava and at Taurene during the monitoring period. This does not agree with the precipitation results, which showed in recent years a considerable increase of pH. That indicates that the sum of anthropogenic and natural acid inputs is still too high to be buffered in the soil (Moffat et al., 2002). Sulphate concentrations in SW were significantly higher compared to BP and TF (Table 2). This enrichment is due to ion leaching from the organic layer, which is related to litterfall, ion exchange reactions, dissolution and weathering processes in the soil, and to the concentration effect of evaporation (Ukonmaanaho & Starr, 2002).

Both at the Rucava, and the Taurene IM stations, $\text{SO}_4\text{-S}$ concentrations in SW significantly increased (Fig. 6).

This does not coincide with the pattern of changes in $\text{SO}_4\text{-S}$ concentration in precipitation (Fig. 4). Therefore it is evident that there is no direct relationship between $\text{SO}_4\text{-S}$ in precipitation and in soil water, as reported in other studies carried out in boreal forests (Moffat et al., 2002). In the largest part of Central European forests sulphur leaching from soil is greater than is deposited from the atmosphere, which within the last decade has decreased. This indicates that soil, under changing environmental conditions, is releasing sulphur stored in the soil in previous episodes of higher sulphate input (Intensive

Monitoring of Forest Ecosystems in Europe. Technical Report, 2001). Similarly to $\text{SO}_4\text{-S}$, the $\text{NO}_3\text{-N}$ concentrations during the observation period in SW at Rucava and Taurene showed a decreasing tendency but this was not statistically significant.

4 Conclusion

Trend analyses indicated that the concentrations of $\text{SO}_4\text{-S}$ in precipitation in Latvian pine forests has markedly declined from 1994–2004. During the same time, a decrease in precipitation acidity was observed. The largest changes were observed in the western part of Latvia, and reflect a decrease of long-range trans-boundary air pollution impact from Western Europe. The deposition of $\text{SO}_4\text{-S}$ derived from BP and TF did not change during the monitoring period. The only statistically significant decreasing trend was found for $\text{SO}_4\text{-S}$ deposition in BP at Taurene. Similarly, also the $\text{NO}_3\text{-N}$ concentrations in precipitation and deposition did not show significant linear trends.

The trend of decreasing $\text{SO}_4\text{-S}$ concentrations and increasing pH in precipitation were not followed by similar changes in soil water. On the contrary, $\text{SO}_4\text{-S}$ concentrations increased and water acidity did not change in SW.

Mean concentrations of $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ increased in the order: BP<TF<SF. This trend in enrichment in throughfall and stemflow is related to wash-off of accumulated dry deposition on surfaces of needles and bark.

The study showed that in pine forests of Latvia in some cases precipitation and soil water chemical composition formation differs from that reported for boreal forests in Scandinavia. This suggests that generalization the impact of environmental pollution on boreal forests extrapolating to the boreo-nemoral forests of Latvia should be done with caution.

Acknowledgements The work was financially supported by the European Union Structural Fund and Latvian Environment, Geology and Meteorology Agency. The authors wish to thank Professor G. Brumelis for his help in preparing the English version of the manuscript. We also thank two anonymous reviewers for their valuable comments.

References

- Beier, C., Eckersten, H., & Gundersen, P. (2001). Nitrogen cycling in a Norway Spruce Plantation in Denmark – A SOILN model application including organic n uptake. *The Scientific World*, 1(S2), 394–406.
- Bredemeier, M. (1988). Forest canopy transformations of atmospheric deposition. *Water, Air and Soil Pollution*, 40, 121–138.
- Bytnerowicz, A., & Fen, M. E. (1996). Nitrogen deposition in California forests: A review. *Environmental Pollution*, 92, 127–146.
- Eichhorn, J., Haussmann, T., Paar, U., Reinds, G. J., & Vries, W. (2001). Assessment of impacts of nitrogen deposition on beech forests: Results from the Pan-European Intensive Monitoring Programme. *The Scientific World*, 1(S2), 423–432.
- Gower, C., Rowell, D. L., Nortcliff, S., & Wild, A. (1995). Soil acidification: Comparison of acid deposition from the atmosphere with inputs from the litter/soil organic layer. *Geoderma*, 66, 85–98.
- Intensive monitoring of forest ecosystems in Europe. Technical Report. (2001). Forest Intensive Monitoring Coordinating Institute. The Netherlands.
- Laivins, M., Lulko, I., & Frolova, M. (1996). Dynamics of precipitation chemical content in Rucava' (In Latvian). *Mežzinātne*, 6(39), 57–66.
- Lee, D. S., Dollard, G. J., Derwent, R. G., & Pepler, S. (1999). Observation on gaseous and aerosol components of atmosphere and their relationships. *Water, Air and Soil Pollution*, 113, 175–202.
- Lindberg, S. E., & Lovett, G. M. (1992). Deposition and forest canopy interactions of airborne sulphur: Results from the integrated forest study. *Atmospheric Environment*, 26A(8), 1477–1492.
- Lindberg, S. E., Lovett, G. M., Richter, D. D., & Johnson, D. W. (1986). Atmospheric depositions and canopy interactions of major ions in a forest. *Science*, 231, 141–145.
- Luttermann, A., & Freedman, B. (2000). Risks to forests in heavily polluted regions. In J. L. Innes & J. Oleksyn (Ed.), *Forest dynamics in heavily polluted regions* (pp. 9–26), Report no. 1 of the IUFRO Task Force on Environmental Change. CABI Publishing, UK.
- Manual for Integrated Monitoring (1998). UN ECE convention on long-range transboundary air pollution. International Co-operative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems. – Finnish Environment Institute, Impacts Research Division, Helsinki.
- Moffat, A. J., Kvaalen, H., Solberg, S., & Clarke, N. (2002). Temporal trends in throughfall and soil water chemistry at three Norwegian forests, 1986–1997. *Forest Ecology and Management*, 168, 15–28.
- Pajuste, K. (2004). Deposition and transformation of air pollutants in coniferous forests. PhD. Thesis, University of Tartu. Estonia, pp. 24–43.
- Parker, G. G. (1983). Throughfall and stemflow in the forest nutrient cycle. *Advances in Ecological Research*, 13, 57–133.
- Schachtschabel, P., Blume, H., Brümmer, G., Hartge, H., & Schwertmann, U. (1989). *Lehrbuch der Bodenkunde*. Stuttgart: Enke Verlag, p. 491.
- Stachurski, A., & Zimka, J. R. (2000). Atmospheric input of elements to forest ecosystems: A method of estimation using artificial foliage placed above rain collectors. *Environmental Pollution*, 110, 345–356.
- Stoddard, J. L., Jeffries, D. S., Lukewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., et al. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature*, 410, 575–578.
- Ukonmaanaho, L. (2001). Canopy and soil interaction with deposition in remote boreal forest ecosystems: A long-term integrated monitoring approach. PhD Thesis, University of Helsinki. Helsinki, pp. 31–52.
- Ukonmaanaho, L., & Starr, M. (2002). Major nutrients and acidity: Budgets and trends at four remote boreal stands in Finland during the 1990s. *Science of the Total Environment*, 297, 21–41.

Acid Rain in Downtown São Paulo City, Brazil

Marcos A. dos Santos · Cynthia F. Illanes ·
Adalgiza Fornaro · Jairo J. Pedrotti

Received: 17 June 2005 / Revised: 15 December 2005 / Accepted: 12 February 2006 / Published online: 19 January 2007
© Springer Science + Business Media B.V. 2007

Abstract During the period from July 2002 to June 2004, the chemical characteristics of the rainwater samples collected in downtown São Paulo were investigated. The analysis of 224 wet-only precipitation samples included pH and electrical conductivity, as well as major ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) and carboxylic acids (acetic, formic and oxalic) using ion chromatography. The volume weighted mean, VWM, of the anions NO_3^- , SO_4^{2-} and Cl^- was, respectively, 20.3, 12.1 and $10.7 \mu\text{mol l}^{-1}$. Rainwater in São Paulo was acidic, with 55% of the samples exhibiting a pH below 5.6. The VWM of the free H^+ was $6.27 \mu\text{mol l}^{-1}$, corresponding to a pH of 5.20. Ammonia (NH_3), determined as NH_4^+ (VWM= $32.8 \mu\text{mol l}^{-1}$), was the main acidity neutralizing agent. Considering that the H^+ ion is the only counter ion produced from the non-sea-salt fraction of the dissociated anions, the contribution of each anion to the free acidity potential has the following profile: SO_4^{2-} (31.1%), NO_3^- (26.0%), CH_3COO^- (22.0%), Cl^- (13.7%), HCOO^- (5.4%) and $\text{C}_2\text{O}_4^{2-}$ (1.8%). The precipitation chemistry showed

seasonal differences, with higher concentrations of ammonium and calcium during autumn and winter (dry period). The marine contribution was not significant, while the direct vehicular emission showed to be relevant in the ionic composition of precipitation.

Keywords acid rain · ionic composition · urban area · wet deposition · air pollution

1 Introduction

In the last two decades, the study of the chemical composition of rainwater samples has increasingly been investigated in several parts of world. This type of research provides useful information on the atmospheric composition, helps identify the potential chemical sources of wet precipitation, and improves the understanding of regional and local air pollution and its effects on the ecosystems. The atmospheric composition is determined by natural sources – mainly oceans and continents – and anthropogenic sources, associated to human activities such as biomass burning (forests and plantations), industrial processes and fossil fuel burning. In several cities of the world, significant changes in atmospheric composition by anthropogenic sources have caused serious environmental problems, among then increasingly degraded air quality.

In the São Paulo metropolitan area (MASP), atmospheric pollutants like SO_2 , CO, NO_x , O_3 and inhalable particulates (PM_{10}) have been measured since 1973 and continuously monitored since 1981 by an automatic network (Martins et al., 2004; CETESB, 2005).

M. A. dos Santos · C. F. Illanes · J. J. Pedrotti (✉)
Departamento de Química,
Universidade Presbiteriana Mackenzie,
Rua da Consolação, 896,
01302-907 São Paulo, SP, Brazil
e-mail: jpedrotti@mackenzie.com.br (J.J. Pedrotti)

A. Fornaro
Departamento de Ciências Atmosféricas,
Instituto de Astronomia,
Geofísica e Ciências Atmosféricas – USP,
Rua do Matão, 1226,
05508-900 São Paulo, SP, Brazil

The results of these measurements have been indicated that the atmospheric emissions in the MASP are linked to pollutants released by industries and mainly, by the large fleet of vehicles.

With reference to liquid phase, there are some studies of rainwater chemistry in the city of São Paulo. Most of this work is restricted to inorganic major ions in rainwater samples collected in the city's west zone (Forti, Moreira-Nordemann, Andrade, & Orsini, 1990; Paiva et al., 1997). In the same sampling site, recent results showed that the organic acids provide a significant contribution to the acidity of rainwater samples (Fornaro & Gutz, 2003). In downtown São Paulo, the first results for major cations and inorganic and organic anions in rainwater samples collected during the end of the winter of 2002 up to the summer of 2003 were described more recently (Leal, Fontenele, Pedrotti, & Fornaro, 2004).

This work presents the chemical composition of wet-only deposition samples collected in downtown São Paulo during a period of two years. The inorganic ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) and organic anions (CH_3COO^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$) were measured by ion chromatography in wet precipitation in order to evaluate the main anthropogenic sources responsible for contamination in the area. The relative contribution of carboxylic acids to the potential free acidity of rainwater is also discussed.

2 Experimental

2.1 Site Sampling

São Paulo city is located in the southeastern region of São Paulo state, Brazil, around 45 km from the coast, at 780 m above the sea level, with an extension area over 1,528 km². The city has 10.5 million inhabitants and it is the largest part of the São Paulo Metropolitan Area (MASP), one of the most populated urban regions in the world, with more than 18 million inhabitants. The main sources of pollution in the city are vehicular and industrial emissions. Diesel, hydrated ethanol and gasohol (gasoline + 25% of ethanol) are the most common fuels used by almost seven million heavy and light vehicles. According to estimates of CETESB (2005), the fluxes of the main pollutants emitted into the atmosphere in the last years have obeyed the following distribution: 1.7 million ton/year

of carbon monoxide (CO), 38,000 ton/year of sulfur oxides (SO_2), 371,000 ton/year of nitrogen oxides (NO_x), 404,000 ton/year of hydrocarbons (HC) and 63,000 ton/year of inhalable particles (PM_{10}). The vehicular fleet has been responsible for 98% of CO, 97% of HC, 96% of NO_x , 55% of SO_2 and 40% of PM_{10} emissions.

Even though studies on the ionic composition of these fuels used in the vehicular fleet of São Paulo city are scarce, Munoz et al (2004) published results of the quantitative determination of inorganic ions in ethanol used, both in the anhydrous (mixed with 75% gasoline) and in hydrated form (94% ethanol) by the car fleet. The analytical determinations carried out by capillary zone electrophoresis showed a significant presence of anions and cations usually found in rainwater samples. Among all the ions, the highest concentration was for NO_3^- ($46.7 \mu\text{mol l}^{-1}$), followed by Na^+ ($34.4 \mu\text{mol l}^{-1}$), K^+ ($14.3 \mu\text{mol l}^{-1}$), Cl^- ($9.0 \mu\text{mol l}^{-1}$) and SO_4^{2-} ($7.9 \mu\text{mol l}^{-1}$), while NH_4^+ , Ca^{2+} and Mg^{2+} were not detected.

2.2 Rainwater Sampling

The rainwater samples were collected within the campus of Mackenzie University, in downtown São Paulo, from July 2002 to June 2004. Wet-only samples were collected with an automatic rainwater collector, model G.K. Walter, installed on the top of the Education Faculty building (around 15 m high). High-density polyethylene flasks were used to store the rainwater during the period of the sampling. The precipitation samples were collected immediately after each rain event or in the early morning following night events. On arrival at the laboratory, each sample was weighed for volume determination. Afterwards, the sample was separated into two of 15 ml aliquots and transferred to high-density polyethylene flasks for different analytical determinations, usually made a week after the rain event. For pH and conductivity measurements, an unfiltered aliquot was preserved at 4°C in a refrigerator, while for chromatographic determination the remaining aliquot was filtered through a 0.22 μm cellulose acetate membrane and stored in a freezer at -18°C.

2.3 Reagents and Instruments

All reagents were of analytical grade (>99% purity) and were used without further purification. Ultra-pure

water used to prepare the solution was obtained from a Barnstead Nanopure system (resistivity $>18 \text{ M}\Omega \text{ cm}^{-1}$). The stock standard solutions (100 mmol l^{-1}), obtained by dissolution of their salts in deionized water, were stored in a refrigerator. The multi-element standard solutions of lower ion concentration were prepared just before their use.

The pH measurements were made with a Digimed DM-20 potentiometer coupled to a glass electrode combined with a Ag/AgCl (saturated in KCl) reference electrode. For conductivity measurements, a Digimed model DM-31 conductivity meter, fitted with a constant 1.0 cm^{-1} cell was used. The conductivity meter was calibrated with 10, 1.0, and 0.1 mmol l^{-1} KCl standard solutions. All pH and conductivity measurements, made in triplicate, were carried out at $25^\circ \pm 0.1^\circ \text{C}$ temperature.

Major cations and anions were determined by a Metrohm chromatograph 761 Compact IC with conductivity detection. Anion and cations determinations were made using Metrohm accessories: a A-Supp 5 ($250 \times 4 \text{ mm}$) separator column with an anion micro-membrane suppressor. For cations, a C2-250 ($250 \times 4 \text{ mm}$) separator column protected by a C-2 guard column was used. The analytical determination of each major ion was made using a calibration plot with a concentration range from 5 to $50 \mu\text{mol l}^{-1}$.

3 Results and Discussion

3.1 Rainwater Features

From July 2002 to June 2004, 224 wet-only precipitation samples were collected. Figure 1 shows the monthly rainfall distribution during the period of study. The amount of rainfall recorded for the period was 2,197 mm, which is 20% below average for the last 30 years, for the same area and period. It shows that most rainfall occurs between October and March (spring and summer months). During this period, the wet precipitation amounted to 1,760 mm, corresponding to 80% of the total rainfall volume collected. The average daily rainfall for the wet period was 9.7 mm d^{-1} , while in the dry period (usually between May and August) it was only 2.4 mm d^{-1} .

In order to verify if major components were measured in the rainwater samples, two quality control criteria were applied: (a) condition of electroneutrality

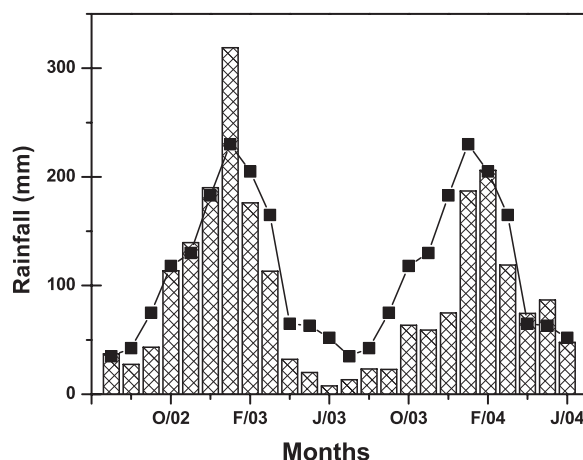


Fig. 1 Historical series (filled square) of monthly precipitation (1973–2003) and monthly profile of rainfall recorded during the study period, July 2002 up to June 2004 (columns). The wet period: October–March; dry period: April–September

(charge balance) and (b) the comparison between the measured conductivity and the calculated conductivity, the latter based on the ionic concentrations measured in each sample. Following these two criteria, 10 samples (4.5%) were rejected. The linear regression analysis between the anions ($\sum_{\text{anions}}^-$) and cations ($\sum_{\text{anions}}^+$) measured showed a good correlation coefficient $r=0.97$ and a slope of 0.97, indicating a slight excess of anions, as illustrated in Fig. 2a. Calculated conductance versus measured conductance (Fig. 2b) showed good concordance, too ($r=0.96$, slope=0.88). These results indicate that chromatography-measured ions and H^+ concentration, obtained from pH values, comprise practically the major of ionic species in rainwater samples collected in downtown São Paulo.

3.2 Chemical Composition

Figure 3 shows box-whisker plots for cations (Fig. 3a) and anions (Fig. 3b) concentrations in 214 rainwater samples. The data show a considerable variation of the concentration of all ions from sample to sample, which is a common characteristic in studies of rainwater chemistry.

The average relative contribution of the ionic species concentration in rainwater follows this order: $\text{NH}_4^+ > \text{NO}_3^- > \text{CH}_3\text{COO}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{Cl}^- > \text{Ca}^{2+} > \text{H}^+ > \text{HCOO}^- > \text{K}^+ > \text{Mg}^{2+} > \text{C}_2\text{O}_4^{2-} > \text{NO}_2^-$.

The precipitation in downtown São Paulo is dominated by the NH_4^+ ion with an average concentration of $43.9 \mu\text{mol l}^{-1}$ representing 49% of all the cationic

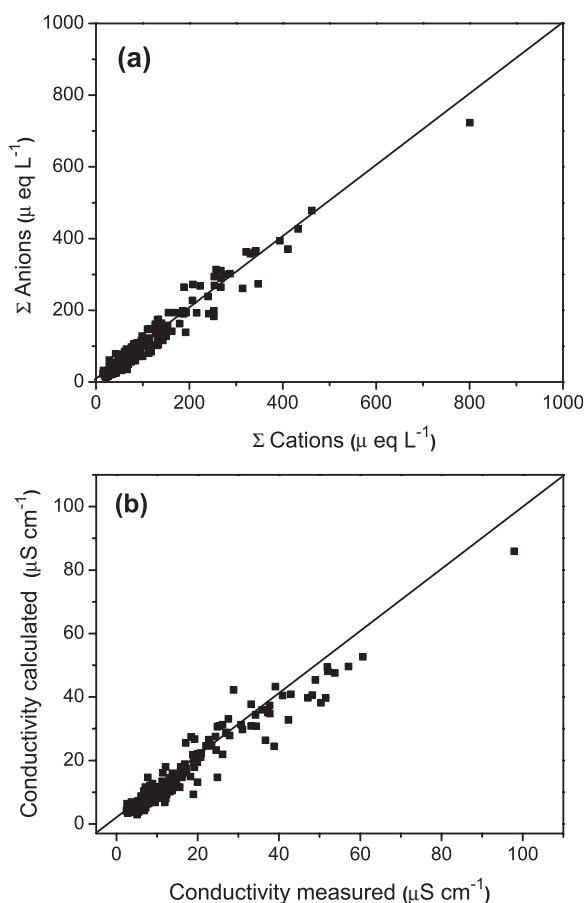


Fig. 2 Ionic balance in rainwater samples ($n=207$): **a** electro-neutrality ($\mu\text{eq l}^{-1}$); **b** Correlation between measured and calculated conductance. The continuous line has been drawn considering a unitary slope

content of the rainwater samples. Similar supremacy was obtained in two other studies carried out in the west region of the city. The next most abundant cations are Na^+ and Ca^{2+} with arithmetic mean concentration of 19.3 and 12.7 $\mu\text{mol l}^{-1}$, respectively. The lower concentrations were measured for free H^+ (7.8 $\mu\text{mol l}^{-1}$), K^+ (5.6 $\mu\text{mol l}^{-1}$) and Mg^{2+} (3.9 $\mu\text{mol l}^{-1}$) ions. These three ions together contribute with approximately 20% of the total cation mass. The Ca^{2+} , K^+ and Mg^{2+} cations in rainwater from São Paulo are usually associated with the resuspension of the dust from the soil and the intensive activities of the construction industry involving the use of cement and gypsum.

Among the anions, nitrate showed the highest arithmetic mean concentration, 27.5 $\mu\text{mol l}^{-1}$. The main anthropogenic source of nitrate in rainwater in urban areas like São Paulo is the oxidation of nitrogen oxides

($\text{NO}_x = \text{NO} + \text{NO}_2$) produced by combustion of fossil fuels used by the vehicular fleet (CETESB, 2005).

The other abundant anions were CH_3COO^- , SO_4^{2-} and Cl^- , with arithmetic mean concentrations of 24.4, 17.0 and 15.3 $\mu\text{mol l}^{-1}$, respectively. These three ions together contribute with 74% of total anion mass. The concentration of HCOO^- was 6.8 $\mu\text{mol l}^{-1}$, which is less than one-fourth of that of acetate. Fornaro and Gutz (2003) discussed acetic and formic acids ratios (A/F) in gas and aqueous phase in São Paulo. They considered that the $\text{A/F} > 1$ ratio is a sign of the predominance of direct emissions (biogenic or/and anthropogenic). In this study, the A/F ratio in rainwater was approximately 3.5, evidencing the weight of direct emissions produced by the large vehicular fleet in this region.

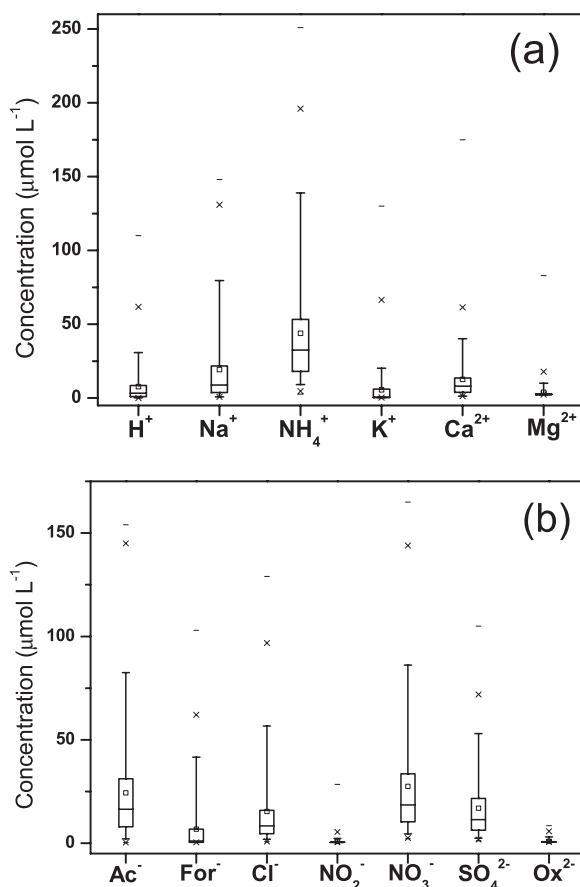


Fig. 3 Box and whisker plots for concentrations of cations **a** and anions **b** in rainwater samples for the period of July (winter) 2002 up to June 2004 (end of the autumn), in São Paulo city. Horizontal box lines: 25, 50 and 75th percentile values; error bars, 5 and 95th percentile values; (x symbol) 1st and 99th percentile; (- sign) minimum and maximum values. The arithmetic mean corresponds to square inside the box

In areas under influence of sea breeze, it is usual to discriminate the marine and continental and/or anthropogenic sources from concentration of major ions. This is frequently made considering Na^+ as the reference element, assuming that all Na content in rainwater is of marine origin. This assumption is usually adopted in studies of rainwater of urban areas due to difficulties to identify sodium sources and the absence of other tracer elements of marine origin. In large urban areas like São Paulo City, this assumption may be susceptible to errors, as it disregards the possible contribution of sodium from crust and anthropogenic emissions. In order to illustrate this fact, studies about inorganic ions of ethanol fuel (consumed by 25% of the vehicular fleet), indicated a Cl/Na ratio of 0.26 (Munoz et al., 2004). Another factor to be remarked in the MASP is related to the contribution of the biomass burning from commercial establishments like pizzerias and bakeries, which use wood as fuel, emitting particles ($\text{PM}_{2.5}$) containing inorganic ions (CETESB, 2005; Ynoue & Andrade, 2004). Considering these difficulties to characterize the sodium sources, the Na content in rainwater samples collected in downtown São Paulo was not evaluated as exclusively from marine origin. Based on this assumption, SO_4^{2-} , Cl^- , Ca^{2+} and Mg^{2+} were also predominantly considered coming from continental/urban sources.

The $\text{C}_2\text{O}_4^{2-}$ was determined in 64% of the rainwater samples, with an arithmetic mean concentration of $0.98 \mu\text{mol l}^{-1}$, while the NO_2^- was the ion with lowest concentration, $0.90 \mu\text{mol l}^{-1}$.

Table 1 shows seasonal differences in VWM concentrations for all species. The concentrations of acidic ions NO_3^- , CH_3COO^- and Cl^- do not show significant differences between the dry and wet period. In the dry period, the VWM concentrations of alkaline ions NH_4^+ and Ca^{2+} increased 11 and 43%, which can explain the decrease of the free H^+ concentration in rainwater samples.

3.3 Profile of Rainwater Acidity

Figure 4 illustrates the frequency distribution of pH. These values range from 4.0 to 7.3, presenting an average of 5.1 and VWM of 5.2. More than 55% of the rainwater samples had pH values <5.6 (resulting from the equilibrium of the pure water with atmospheric CO_2), and nearly 34% of the samples fell within the pH range of 5.0–5.5, indicating that the

Table 1 Data of the VWM concentrations of the ionic components in different seasons

Ions	Dry period VWM ($\mu\text{mol l}^{-1}$)	Wet period	Annual
CH_3COO^-	16.4	17.4	17.1
HCOO^-	6.31	3.51	4.21
Cl^-	10.9	10.7	10.7
NO_2^-	0.74	0.48	0.55
NO_3^-	19.7	20.4	20.2
SO_4^{2-}	13.4	11.6	12.1
$\text{C}_2\text{O}_4^{2-}$	1.00	0.60	0.70
Na^+	10.8	14.4	13.5
NH_4^+	36.3	31.5	32.7
K^+	4.55	3.55	3.81
Ca^{2+}	10.6	6.31	7.39
Mg^{2+}	3.04	3.20	3.16
H^+	4.94	6.74	6.29

precipitation in downtown São Paulo is slightly acidic. On the other hand, around 4% of rainwater samples had pH values higher than 7.0, suggesting the significant contribution of alkaline species to wet precipitation in this region. The pH results obtained in this study are slightly higher than those of other studies of rainwater carried out in the west region of São Paulo, where the pH average values ranged from 4.5–5.0 (Paiva et al., 1997). In comparison with others large cities around the world, the average pH from this study was similar to Rio de Janeiro, 5.12 (de Mello, 2001); higher than the average pH of Mexico City, 4.65 (Baez, Belmont, & Padilla, 1996), Los Angeles, 4.67 (Kawamura, Steinberg, & Kaplan, 1996) and Seoul, 4.7 (B. K. Lee, Hong, & D. S. Lee, 2000) but much lower than Madrid, 6.6 (Hontoria et al., 2003).

The relative contribution of each anion to the potential free acidity, PFA, of a rainwater sample was determined by using the following equation:

$$\text{PFA} = \frac{[\text{X}]}{\sum \text{anions}}$$

where [X] is the individual VWM concentration ($\mu\text{mol l}^{-1}$) of the anion multiplied by the number of hydrogen atoms that are produced in the ionization process,

$$\begin{aligned} \sum_{\text{anions}} &= [\text{Cl}^-] + [\text{NO}_3^-] + [\text{CH}_3\text{COO}^-] \\ &+ [\text{HCOO}^-] + 2x[\text{SO}_4^{2-}] + 2x[\text{C}_2\text{O}_4^{2-}] \end{aligned}$$

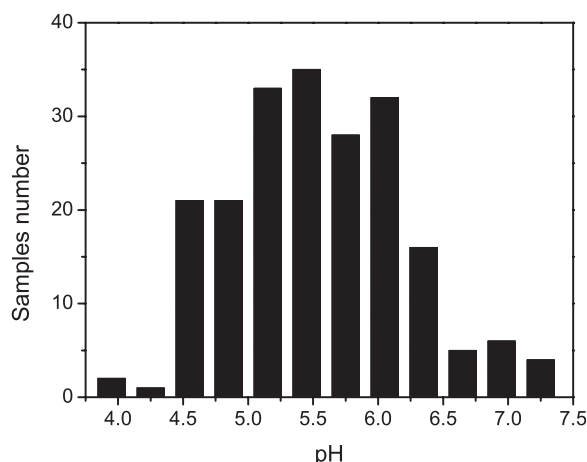


Fig. 4 Histogram for pH in wet-only deposition samples in São Paulo

All weak acids are appreciably dissociated at the pH range found in rainwater samples of downtown São Paulo. At pH value of 5.2, obtained from VWM of free H^+ , the acetic ($K_a = 1.75 \times 10^{-5} \text{ mol l}^{-1}$), formic ($K_a = 1.77 \times 10^{-4} \text{ mol l}^{-1}$) and oxalic ($K_{a1} = 5.59 \times 10^{-2}$ and $K_{a2} = 5.42 \times 10^{-5} \text{ mol l}^{-1}$) acids are 74, 97 and 99% dissociated, respectively (Harris, 1998). Considering this fact, all organic acids were included in the evaluation of PFA.

The results of the relative contribution of each inorganic and organic acids to the potential free acidity in wet precipitation in downtown São Paulo is presented in Table 2. The relative participation of inorganic acids is high (71%) while that of organic acids is 29%. Considering only the organic acids, their contribution in PFA obtained in the present study was comparable to the results obtained in Los Angeles (Kawamura et al., 1996), but lower in relation to the work developed in the west region of São Paulo (44%) during the period of February to October 2000 (Fornaro & Gutz, 2003). However, besides the differences in periods and region of São Paulo, the rainwater sampling in 2000 was restricted to autumn and winter seasons.

If we consider the concentration of all major anions (Cl^- , NO_3^- , CH_3COO^- , $HCOO^-$, SO_4^{2-} , $C_2O_4^{2-}$) in rainwater composition and assuming that they are in the form of free acids (completely ionized), the sum of the VWM concentrations of these chemical species should produce a precipitation with a pH of 4.1, which is lower than the pH measured, 5.2. The significant

Table 2 Contribution of the inorganic and organic acids to the potential free acidity of the wet only deposition

Species	Potential free-acidity (%)
CH_3COOH	22.0
$HCOOH$	5.40
HCl	13.7
HNO_3	26.0
H_2SO_4	31.1
$H_2C_2O_4$	1.80

difference is an indication that alkaline species like NH_3 and calcium carbonate or hydroxide are neutralizing the action of the acids.

From the difference of the sum of the VWM concentrations of SO_4^{2-} , CH_3COO^- and NO_3^- , and the free H^+ VWM concentration, it was possible to estimate that around 90% the SO_4^{2-} , CH_3COO^- and NO_3^- are in neutralized form. In order to determine which cations (NH_4^+ , Ca^{2+} , Mg^{2+} or K^+) more frequently contribute to neutralize the free potential acidity, a neutralization factor (NF) described by Kulshrestha, Sarkar, Srivastava, & e Parashar (1995), which uses the ratio of cations over anions [NH_4^+ , Ca^{2+} or Mg^{2+}]/[$NO_3^- + SO_4^{2-}$], was applied. In view of the significant CH_3COO^- concentration determined in the chemistry composition of the rainwater in this study, the neutralization factor was calculated using the following equation:

$$NFx_i = \frac{[x_i]}{[NO_3^-] + [CH_3COO^-] + [SO_4^{2-}]}$$

where x_i are the cation of interest, and all the ionic concentrations are expressed in $\mu\text{mol l}^{-1}$.

Table 3 presents the results of the NF of the major ions. Ammonium was the main neutralizing component followed by calcium ion. These two ionic species were responsible for 86% of all nitrates, acetates and sulfates measured in rainwater of downtown São Paulo. Potassium and magnesium provided a minor contribution to the neutralization process.

A comparison between the values of NF obtained in the present study with results found in Madrid, Spain, shows that calcium contributed 64% to the neutraliza-

Table 3 Neutralization factor of the major ions in the rainwater samples

	$[\text{NH}_4^+]/\sum \text{anions}$	$\text{Ca}^{2+}/\sum \text{anions}$	$\text{Mg}^{2+}/\sum \text{anions}$	$\text{NF}/\sum \text{anions}$
Minimum	0.14	0.017	0.015	0.003
Maximum	2.0	0.62	0.48	0.52
Mean	0.68	0.18	0.07	0.07
<i>Sd</i>	0.30	0.12	0.05	0.010

Obs: *Sd* standard deviation; $\sum \text{anions} [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{CH}_3\text{COO}^-]$

tion process, while ammonium contributed only 7% (Hontoria et al., 2003). The significant difference can be attributed to high calcium VWM concentration ($195 \mu\text{mol l}^{-1}$) measured in the precipitation of this Spanish city. Data from the chemical composition of rainwater in these two large cities show that VWM ammonium concentration was approximately 27% lower in downtown São Paulo, while the VWM calcium concentration in Madrid was 26 times higher than that of the present study.

4 Conclusions

Rainwater samples were collected during 720 days (July 2002–June 2004) in downtown São Paulo to study the chemical composition of the precipitation. Ammonium was the dominant ion, followed by nitrate, acetate, sodium and sulfate. These five ions represent 69% of the ionic content of the rainwater samples.

The average value of pH was 5.11 (VWM, pH=5.20). The frequency distribution of pH showed that 55% of rainwater samples presented pH value lower than 5.6. The acidity of rainwater originates from a mixture of inorganic and organic acids, the organic acids (CH_3COOH , HCOOH e $\text{H}_2\text{C}_2\text{O}_4$) being responsible for 29.2% of the potential acidity of the rainwater. Ammonia was the main neutralizing agent of the wet precipitation, followed by calcium carbonate or calcium hydroxide (from partial dissolution of cement dust). The significant participation of these alkaline chemical species to the neutralization of the nitric, acetic and sulfuric acids can explain the slight acidity of the rainwater collected in downtown São Paulo.

The precipitation chemistry showed some seasonal differences, with an increase of VWM concentrations of ammonium and calcium during dry periods. The rainwater in downtown São Paulo is greatly influ-

enced by local sources of air pollutants, particularly the large vehicle fleet and the significant construction industry activity.

Acknowledgments The authors are grateful to Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) and Fundo Mackenzie de Pesquisa (MACKPESQUISA) for financial support.

References

- Baez, A. P., Belmont, R. D., & Padilla, H. G. (1996). Chemical composition of precipitation at two sampling sites in Mexico: A 7-year study. *Atmospheric Environment*, 31, 915–925.
- CETESB (2005). Relatório de Qualidade do Ar no Estado de São Paulo – 2004, Secretaria do Meio Ambiente, Série Relatórios, ISSN 0103-4103, São Paulo (<http://www.cetesb.sp.gov.br>).
- de Mello, W. Z. (2001). Precipitation chemistry in the coast of the Metropolitan Region of Rio de Janeiro, Brazil. *Environmental Pollution*, 114, 235–242.
- Fornaro, A., & Gutz, I. G. R. (2003). Wet deposition and related atmospheric chemistry in the São Paulo metropolis, Brazil: Part 2. Contribution of formic and acetic acids. *Atmospheric Environment*, 37, 117–128.
- Forti, M. C. Moreira-Nordemann, L. M., Andrade, M. F., & Orsini, C. Q. (1990). Elements in the precipitation of S. Paulo city (Brazil). *Atmospheric Environment*, 24, 355–360.
- Harris, D. C. (1998). *Quantitative chemical analysis* (p. 899). New York: W.H. Freeman and Company.
- Hontoria, C., Saa, A., Almorox, J., Cuadra, L., Sánchez, A., & Gascó, J. M. (2003). The chemical composition of precipitation in Madrid. *Water, Air Soil Pollution*, 146, 35–54.
- Kawamura, K., Steinberg, S., & Kaplan, I. R. (1996). Concentrations of monocarboxylic and dicarboxylic acids in southern California wet precipitations: Comparison of urban and nonurban samples and compositional changes during scavenging. *Atmospheric Environment*, 30, 1035–1052.
- Kulshrestha, U. C., Sarkar, A. K., Srivastava, S. S., & e Parashar, D. C. (1995). Wet-only and bulk deposition studies at New Delhi (India). *Water Air Soil Pollution*, 85, 2137–2142.

- Leal, T. F. M., Fontenele, A. P. G., Pedrotti, J. J., & Fornaro, A. (2004). Composição iônica majoritária de águas de chuva na região central de São Paulo. *Química Nova*, 27(6), 855–861.
- Lee, B. K., Hong, S. H., & Lee, D. S. (2000). Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula. *Atmospheric Environment*, 34, 563–575.
- Martins, M. H. R. B., Anazia, R., Guardani, M. L. G., Laçava, C. I. V., Romano, J., & Silva, S. R. (2004). Evolution of air quality in the São Paulo metropolitan área and its relation with public policies. *International Journal Environment and Pollution*, 22(4), 430–440.
- Munoz, R. A. A., Richter, E. M., Jesus, D. P., Lago, C. L., & Angnes, L. (2004). Determination of inorganic ions in ethanol fuel by capillary electrophoresis. *Journal of the Brazilian Chemical Society*, 15(4), 523–526.
- Paiva, R. P., Pires, M. A. F., Munita, C. S., Andrade, M. F., Gonçalves, F. L. T., & Massambani, O. (1997). A preliminary study of the anthropogenic contribution to São Paulo rainfall. *Fresenius Environmental Bulletin*, 6, 508–513.
- Ynoue, R. Y., & Andrade, M. F. (2004). Size-resolved mass balance of aerosol particles over the São Paulo Metropolitan Area of Brazil. *Aerosol Science and Technology*, 38 (S2), 1–12.

Atmospheric Metal Pollutants-Archives, Methods, and History

Stephen A. Norton

Received: 17 June 2005 / Revised: 10 January 2006 / Accepted: 12 February 2006 / Published online: 13 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Pollution of the atmosphere with cadmium (Cd), mercury (Hg), and lead (Pb) is a consequence of human activities. Natural archives are necessary to reconstruct the long-term history of metal deposition because accurate measurement of atmospheric deposition is a recent accomplishment. Reconstructions require: (1) accurate determination of concentrations of elements and isotopes, (2) accurate chronology of archives, and (3) archives that faithfully record atmosphere deposition. The most useful long-term archives are accumulations of ice and snow, peat, and lake sediment. Quantification of Cd deposition is uncommon because of its low concentration and substantial chemical mobility. Nonetheless, trends in peat and lake sediment are similar to those of Hg and Pb since ca. 1800 A.D. Both Hg and Pb are relatively chemically immobile and thus the peat and lake archives are believed to record historic trends of atmospheric deposition. Isotopic and concentration studies of Pb indicate a history of northern hemisphere atmospheric pollution extending back prior to 0 A.D. Although measurements of Hg concentration are now routine, isotopic measurements are in their infancy. Some Hg pollution sources have unique isotopic ratios, thereby contributing unique signals to the total

Hg. Maximum accumulation rates of Hg and Pb occur up to 10 years later than for Cd (1970s versus 1960s in eastern North America, perhaps slightly later in Europe). By 2004, deposition of Cd, Hg, and Pb had declined from peak values in eastern North America more than 75, 75, and 90%, respectively.

Keywords atmospheric pollution · archives · cadmium · ice · lake sediment · lead · mercury · peat

1 Introduction

“What goes up, must come down” (somewhere). The atmosphere has been a conduit for chemicals for all of geologic time. Many components in the atmosphere are variable in concentration, exist in different phases (solid, liquid, or gas), and have relatively short residence times. The entire periodic table passes through the atmosphere, naturally. Sources include soil dust, vegetation exudates, soil degassing, volcanism, marine aerosols, and release of gases from wetlands and the oceans. Human activity has increased the atmospheric flux of virtually the entire periodical table to the point that, for most elements, atmospheric fluxes are dominated by human-induced processes. Increased emissions to the atmosphere are caused primarily from land clearance, agriculture, biomass fires, fossil fuel consumption, smelting of ores, and transportation. The residence time (and thus travel distance) of substances emitted to the

S. A. Norton (✉)
Department of Earth Sciences,
Bryand Global Sciences Center, University of Maine,
Orono, ME 04469-5790, USA
e-mail: Norton@Maine.Edu

atmosphere relates to phase state (solid, liquid, or gas) and deposition mechanisms. Many of the emissions are benign, some are not. The focus of this paper is the recent history of three elements (cadmium [Cd], lead [Pb], and mercury, [Hg]) that are viewed as pollutants because their fluxes to and from the atmosphere produce concentrations that may be injurious to ecosystems, and especially to humans. Consequently they have been seriously studied over several decades. In addition to concerns of ecological health, the study of atmospheric deposition of Cd, Hg, and Pb has four objectives:

1. What is the chronology of atmospheric pollution, including onset, maximum values, and trends?
2. What is the modern magnitude of atmospheric pollution and how does it vary spatially?
3. What are (were) the absolute atmospheric deposition rates?
4. What are (have been) the sources of atmospheric pollution?

2 Sources of Data

Since the 1950s, chemical analytical methods for trace metals have evolved from atomic absorption flame spectrometry to inductively coupled plasma spectrometry (ICP emission and absorption modes), and inductively coupled plasma mass spectrometry (ICP-MS). Detection limits have been lowered by three to four orders of magnitude and isotopic characterization of many types of environmental samples is possible.

Major developments in dating relatively young archives of atmospheric deposition have occurred. Ice cores are routinely chemically analyzed at sub-annual resolution to determine seasonal chemical variability (Legrand & Mayewski, 1997). Annual layers can be counted back in time. Chronostratigraphic markers (e.g., volcanic dust, excess sulfate [SO₄] from volcanism, and thermo-nuclear bomb fallout) enable verification of more continuous dating methods. Peat cores are routinely dated with ¹⁴C AMS dating for periods in excess of a few hundred years, and with ²¹⁰Pb methods for the last few hundred years (Turetsky, Manning, & Wieder, 2004). “Bomb pulse” dating (1963 and younger) has been applied to some peat records. Ages between about 1800 and 1000 A.D.

are poorly defined. Chronostratigraphic markers (volcanic ash, pollen taxa, etc.) are of limited use. Lake sediments are routinely dated with ²¹⁰Pb methods back to about 1800 (Appleby et al., 1986). Continuous age dating is possible if varves are present. Useful chronostratigraphic markers include exotic pollen, changes in pollen frequency, and bomb fallout stratigraphy. Pollution records with a known chronology for a region can be used for secondary dating.

Monitoring of wet precipitation for the deposition of metals is a relatively recent activity. Networks established in the 1960s and 1970s were spatially restricted, and field and analytical methods led to low quality data. This situation has changed. Some analytes are now monitored at high frequency, even on an event basis, and on a sub-continental scale. For example, Hg in wet deposition is monitored weekly in the United States at 85 stations (<http://www.NADP.sws.uiuc.edu>).

However, measurement of wet deposition (rain, snow, sleet, hail) seriously underestimates the total atmospheric deposition that includes dry deposition. Consequently, assessing the relative influence of human activity on trends in atmospheric deposition is difficult.

Metal concentrations in contemporary natural samples include upper soil horizon surveys (that define spatial variability), and repeated soil surveys that crudely document trends in atmospheric deposition. For example, Evans, Norton, Fernandez, Kahl, and Hanson (2005) demonstrated a significant decline in atmospheric deposition of Cd, Hg, and Pb in sub-alpine soils along a 500 mile transect in eastern North America, between 1979 and 1998. Poikolainen, Kubin, Piispanen, and Karhu (2004) demonstrated substantial declines in the deposition of Cd, Hg, and Pb between 1985 and 2000 over the length of Finland. Unfortunately, these studies do not enable us to reconstruct atmospheric deposition rates, although attempts have been made at measuring the efficiency of capture of deposition by archives. Surveys of foliage, bark, and even woody tissue yield highly variable results, spatially and temporally.

Longer-term data, commonly with poor resolution and poor chronology, have been determined from soil cores (e.g., Renberg, Brännvall, Bindler, & Empteryd, 2000), flood plain sediments (Rognerud, Hongve, Fjeld, & Ottesen, 1999), and even marine marsh and near-shore sediments.

The most useful archives for documenting changing atmospheric pollution include snow (for recent

accumulation) and ice cores (for time scales from hundreds of years to hundreds of thousands of years), peat accumulations (for time scales up to 14,000 years before the present (BP) in glaciated terrain and longer in un-glaciated areas), and lake sediments (time scales as for peat). Measurement of metal accumulation rates in these archives is most useful for reconstruction of trends, not absolute atmospheric deposition rates.

- 2.1 Snow and ice cores may provide high resolution stratigraphy with no chemical matrix problems for chemical interferences. In spite of obvious redistribution and metamorphism of snow prior to its becoming part of an undisturbed ice stratigraphy, very fine chemical records apparently are preserved (Legrand & Mayewski, 1997). Chronological control is commonly excellent in snow and ice cores, using the counting of seasonal or annual cyclical chemical or isotopic changes in cores and using chronostratigraphic markers such as volcanic ash layers (Zielinski, Mayewski, Meeker, Whitlow, & Twicker, 1996). However, snow and ice cores are not as widely distributed as lake sediment or peat records, and are distant from many human activities, with consequently low concentrations of pollutants. The relationship between atmospheric deposition and accumulation rates for metals are likely even more erratic than for lakes and peat, because of climate variability, snow metamorphism, and physical redistribution of snow.
- 2.2 Ombrogenic bogs receive all their nutrients and pollutants from the atmosphere. No watershed is involved for delivery of pollutants to the site of peat accumulation. Thus, if a pollutant is accumulated conservatively (neither lost nor gained from the strata in which it is initially deposited), an archive exists of changing atmospheric deposition of pollutants. Shortcomings include establishing that (1) pollutants are not chemically mobile in the peat and (2) deposition of pollutants is some linear function of atmospheric chemistry.
- 2.3 Sediments in lakes with appropriate bathymetry, hydrology, and chemistry may provide relatively continuous and high resolution chemical records of atmospheric chemistry changes. Shortcomings include (1) difficulty of deconstructing measured chemical changes in terms of watershed effects versus atmospheric change and (2) dilution of atmospheric chemical changes by normal sediment.

3 Analysis of Data

The chemistry of pollution stored in archives can be presented at three levels of understanding:

- 3.1 *Concentration of the pollutant versus time* provides the least information because the concentration of a pollutant is a function of net preservation of the pollutant and dilution by the archive matrix. Nonetheless, in systems that are at steady state through time (net accumulation rate of archive is constant), concentration data enable determination of trends of atmospheric deposition. Enrichment factors (e.g., Shotyk, Krachler, Martinez-Cortizas, Cheburkin, & Emons, 2002) can reveal relative increases in fluxes through time, but not absolute fluxes. Isotopic characterization may enable identification of unique sources of atmospheric pollution.
- 3.2 *Accumulation rate of the pollutant versus time* eliminates the matrix dilution effects but still presents the dilemma of the faithfulness of preservation of a depositional record.
- 3.3 *Correction of accumulation rate of the pollutant for various processes that control the net accumulation rate* (e.g., focusing in lakes; Perry, Norton, Kamman, Lorey, & Driscoll, 2005; diagenesis of sediment; Alfaro-De la Torre & Tessier, 2002) enables the derivation of values closer to actual atmospheric deposition.

4 Case Studies

As a consequence of human activity, particularly since the beginning of the industrial era, the flux of most elements through the atmosphere has been significantly increased. Pollutants receiving study range from A (arsenic) to Z (zinc)! The relative increase in flux of many is relatively minor. However, three elements (cadmium, Cd; lead, Pb; and mercury, Hg) are singled out here because: (1) They are biologically active and have demonstrated negative effects on ecosystem health, and humans in particular; (2) Atmospheric deposition has been dominated by human influence over the past few centuries; and (3) Biogeochemical cycling in many aquatic and terrestrial systems is now dominated by the atmospheric inputs of these elements. The focus here is on the past

few centuries, as recorded by sediment in two lakes in the northeastern USA.

Sargent Mountain Pond (henceforth SMP), Maine, USA (44.334° N, 68.270° W, 336 masl) is a flat-bottomed, 2 ha lake in a glacially scooped basin with thin or absent soils. Abundant exposed bedrock is granite. There is little mineral or organic soil in the watershed that might delay atmospheric chemical changes from being quickly recorded in the sediment. The major element and organic concentrations within the core are relatively constant through time, suggesting little disturbance. The outlet is not permanent.

Spectacle Pond (henceforth SP) is a flat-bottomed seepage lake in eastern Massachusetts, USA (42.55° N, 71.50°W, 80 masl). The basin is in granitic sand and gravel outwash, and has one small inlet and no surface outlet.

Cores were retrieved using a piston corer in 1999 (SP) and 2004 (SMP) and dated with ^{210}Pb . Sediment focusing is minor, based on normal unsupported ^{210}Pb activity/area of sediment in both cores. The sediment record of both lakes should be responsive to changes in atmospheric deposition. The anomalous accumulation rate spikes about 1910 for both lakes are caused by an unusually low ^{210}Pb activity (SP) and by low water content over several intervals (SMP).

4.1 Cadmium – Hemispheric Cd pollution for the last few centuries has been demonstrated qualitatively (concentration changes) using chemistry of ice and snow cores from Greenland (Boutron, Candelone, & Hong, 1995), and peat from Switzerland (Shotyk et al., 2002). Lake sediments have received intense study since about 1980 (e.g., Evans, Smith, & Dillon, 1983). More recent studies (Alfaro-De la Torre & Tessier, 2002; Norton, Wilson, Handley, & Osterberg, in press) indicate that much of the paleolimnological literature is based on data gathered at the time when atmospheric deposition was at or near peak values. Cd concentrations increased early in the 1800s, accelerated dramatically after 1900 to a peak about 1970, and then declined nearly to background by 2000. Surface sediments are slightly enriched in Cd, possibly as a result of recent sediment disturbance in the lake, or the existence of a transient enrichment that disappears during diagenesis. The anthropogenic accumulation rates (Cd_A) (calculated based on the Cd background accumulation rate, changes in sedimentation rate, and focusing) parallel concentration, clearly indicating that atmospheric

deposition of Cd at these sites has declined dramatically over the last 30 years (Table 1). A similar trend was reported by Alfaro-De la Torre and Tessier (2002) for central Quebec, Canada and Norton, Perry, Haines, and Dieffenbacher-Krall (2004) for eastern Massachusetts, USA, indicating a regional signal. Assuming that Cd (and Pb and Hg) pollution pre-dates 1800, as peat, lake, and ice cores suggest, then the concentration enrichment factors and accumulation enrichment factors calculated for these two lakes (Table 1) are conservative estimates (and accurate only for the time spanned by the ^{210}Pb dating) but the timing of maxima is correct, within the errors associated with the ^{210}Pb dating (Fig. 1).

4.2 Lead – Lead is perhaps the best studied of all pollutant metals. Lead behaves conservatively, as indicated by watershed Pb budgets, and isotope studies of peat, soil, and lake sediment. Studies of the concentration and isotopes of Pb in ice cores (Boutron et al., 1995), and peat and lake sediments (Renberg et al., 2000) indicate unequivocally that Pb pollution pre-dates 0 A.D. and has a complex history of increases and declines up to the industrial revolution (ca. 1750 A.D. in Europe and 1850 in North America). Pollution increased strongly thereafter and, because of the introduction of Pb additives to gasoline in the 1920s, peaked about 1970 in North America, slightly later in Europe. With the phasing out of Pb in gasoline and introduction of other emission controls, atmospheric deposition of Pb has declined dramatically into the 21st century (Fig. 2; Table 1). The similarity of timing for Sargent Mountain Pond and Spectacle Pond, separated by 300 km, suggests a regional pollution, as for Cd. This decline has been recorded

Table 1 Enrichment factors (concentrations and accumulation rates for total metals) for Spectacle Pond (SP), Massachusetts and Sargent Mountain Pond (SMP), Maine, USA based on sediment dated by ^{210}Pb

	Maximum conc.	Maximum conc./ conc. enrichment, and year ()	Maximum accum./ accum. enrichment, and year ()
Cd-SP	1.7 ug/g	3.7 (1980)	10.8 (1974)
Cd-SMP	4 ug/g	9.8 (1968)	5.5 (1975)
Pb-SP	210 ug/g	36 (1982)	90 (1980)
Pb-SMP	194 ug/g	39 (1968)	39 (1975)
Hg-SP	527 ng/g	4.79 (1980)	5 (1972)
Hg-SMP	624 ng/g	2.9 (1962)	6.7 (1983)

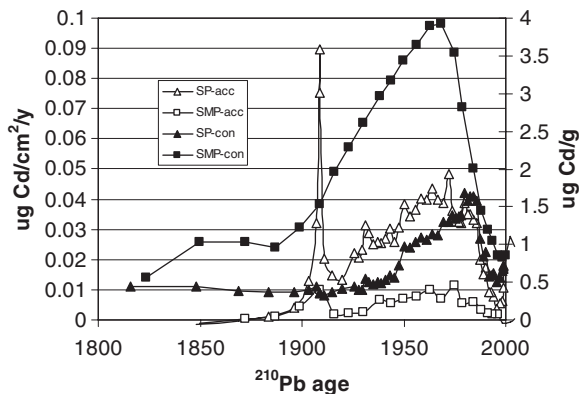


Fig. 1 Concentrations (filled symbols) and accumulation rates (anthropogenic component) (open symbols) of Cd from ^{210}Pb -dated sediment cores from Sargent Mountain Pond (SMP) (squares), Maine, and Spectacle Pond (SP) (triangles), Massachusetts, USA

by atmospheric chemistry measurements, and other archives (e.g., Evans et al., 2005).

- 4.3 Mercury** – Mercury is a particularly nefarious pollutant because of the very complex chemical, physical, and biological controls on its speciation and abundance in the atmosphere, hydrosphere, and biosphere. Mercury, by itself, is not the culprit; but it is a necessary ingredient for the production of methyl Hg. Methyl Hg, typically 1 to 10% of total Hg in aquatic environments, becomes biomagnified in the food chain, starting with phytoplankton. The consequence is that fish and fish predators may ingest tissue with more than 1 mg methyl Hg/kg, a magnification of approximately 10^6 , by weight. Mercury appears to be relatively conservative in peat, although uncertainties remain about what fraction of atmospherically deposited Hg is re-

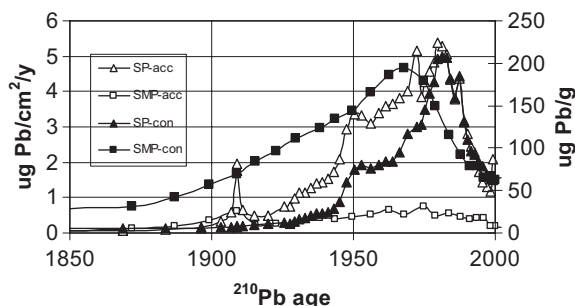


Fig. 2 Concentrations (filled symbols) and accumulation rates (anthropogenic component) (open symbols) of Pb from ^{210}Pb -dated sediment cores from Sargent Mountain Pond (SMP) (squares), Maine, and Spectacle Pond (SP) (triangles), Massachusetts, USA

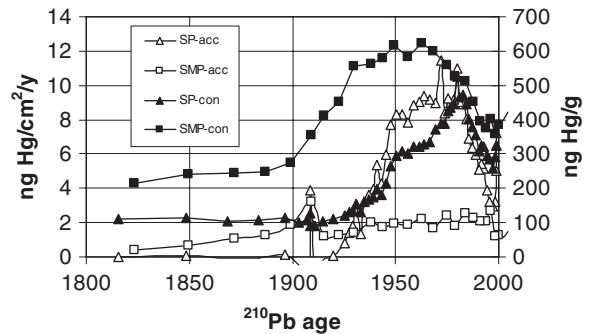


Fig. 3 Concentrations (filled symbols) and accumulation rates (anthropogenic component) (open symbols) of Hg from ^{210}Pb -dated sediment cores from Sargent Mountain Pond (SMP) (squares), Maine, and Spectacle Pond (SP) (triangles), Massachusetts, USA

emitted as Hg vapor or lost in dissolved form. Interestingly, Hg pollution is the least of the three metals, by 2 (Cd) to 3 (Pb) orders of magnitude. Natural values of Hg recorded in archives are not substantially different from values that produce methyl Hg at problematic concentrations. Mercury deposition to bogs over the last 10,000 years has been well-studied (e.g., Bindler, Klarqvist, Klaminder, & Förster, 2004). The consistent findings are that Hg concentration and accumulation in peat vary considerably, spatially and temporally, prior to any conceivable pollution by human activity. For example, at Caribou Bog, Maine, a single long core bottoms in gyttja (lake sediment), transitions upward into fen sediments, and finally to ombrotrophic peat. Hg accumulation was 1–2 $\mu\text{g Hg/m}^2/\text{y}$ during the lake period, 5–10 $\mu\text{g Hg/m}^2/\text{y}$ during much of the fen period, and then declined to < 1 $\mu\text{g Hg/m}^2/\text{y}$ during the bog period, which lasted over 5,000 years. Only in the period 1960–1980 A.D. did Hg accumulation rates exceed those of 5,000 to 10,000 years before present (Ross-Barracough, Givélet, Shotyk, & Norton, 2006). Changes in vegetation caused changes in interception (and thus dry deposition) of atmospheric Hg and these vegetation changes appear to be the most important determinant of “background deposition”. Deposition of Cd and Pb would be similarly affected. However, peat records from dozens of localities and many lakes record a substantial increase in Hg accumulation rates over the last two centuries, peak accumulation between 1960 and 1980, followed by a decline in those archives unaffected by watersheds.

The concentrations of Hg are similar in SMP and SP (Fig. 3). However, the anthropogenic accumulation rate is substantially higher at SP, because of a higher sediment accumulation rate. The histories of accumulation of *anthropogenic* Cd and Hg (total accumulation corrected for background, focusing, and variable sedimentation rate) have the same general trends as their concentrations. Slight differences in trends and peaks may be due to errors in dating and real differences caused by location.

5 Summary

Wherever we look in the northern hemisphere in appropriate archives (ice, peat, and lake sediment) we find compelling evidence of air pollution extending back for several millenia for Cd, Hg, and Pb. Pollution peaked in the period 1965–1975. Since then, atmospheric deposition declined by as much as 75, 75, and 95% by 2000, as recorded by peat and lake sediments, and is now approaching pre-industrial values. The atmosphere at a sub-continental scale is cleaner now than at any time in the last 75–100 years, a clear indication that if we understand the consequences of our past atmospheric emission practices, we can act responsibly eliminate the problem. Although much pollutant Cd, Hg, and Pb still resides in soils of watersheds, the flux of these metals through aquatic ecosystems to lakes, as measured by lake sediment archives, has peaked and in many cases declined. Things are looking up.

Acknowledgments I am very grateful to many colleagues who have engaged me in many discussions about archives of metal pollution. Paul Mayewski and Karl Kreutz (University of Maine) have carefully explained the world of snow and ice cores. Richard Bindler (University of Umeå), Ronald Davis (University of Maine), Eville Gorham (University of Minnesota), and William Shotyk (University of Heidelberg) have been very helpful in developing my understanding of how bogs work. Peter Appleby (University of Liverpool), André Tessier (INRS-Eau), and Josef Veselý (Czech Geological Survey) have helped me understand many aspects of lake sediment chemistry and chronology. I draw heavily on their work, and especially that of my students. This is Maine Agricultural Experiment Station Publication 2849.

References

Alfaro-De la Torre, C. M., & Tessier, A. (2002). Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. *Geochimica et Cosmochimica Acta*, 66, 3549–3562.

- Appleby, P. G., Nolan, P. J., Gifford, D. W., Godfrey, M. J., Oldfield, F., Anderson, N. J., et al. (1986). ^{210}Pb dating by low background gamma counting. *Hydrobiologia*, 143, 21–27.
- Bindler, R., Klarqvist, M., Klaminder, J., & Förster, J. (2004). Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Storre Mosse, Sweden. *Global Biogeochemical Cycles*, 18, 11.
- Boutron, C. F., Candelone, J.-P., & Hong, S. (1995). Greenland snow and ice cores: Unique archives of large scale pollution of the troposphere of the northern Hemisphere by lead and other heavy metals. *Science of the Total Environment*, 160/161, 233–241.
- Evans, G. C., Norton, S. A., Fernandez, I. J., Kahl, J. S., & Hanson, D. (2005). Changes in concentrations of major and trace metals in northeastern U.S.-Canadian sub-alpine forest floors. *Water, Air, and Soil Pollution*, 1(163), 245–267.
- Evans, H. E., Smith, P. J., & Dillon, P. J. (1983). Anthropogenic zinc and cadmium burdens in sediments of selected southern Ontario lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 40, 570–579.
- Legrand, M., & Mayewski, P. (1997). Glaciochemistry of polar cores: A review. *Reviews of Geophysics*, 35, 219–243.
- Norton, S. A., Perry, E., Hanes, T. A., & Dieffenbacher-Krall, A. (2004). Paleolimnological assessment of grove and plow shop ponds, Fort Devens-Ayer, Massachusetts. *Journal Environmental Monitoring*, 4, 457–465.
- Norton, S. A., Wilson, T., Handley, M., & Osterberg, E. C. (in press). Atmospheric deposition of cadmium in the northeastern USA. *Water, Air, and Soil Pollution*.
- Perry, E., Norton, S. A., Kamman, N. C., Lorey, P. M., & Driscoll, C. T. (2005). Deconstruction of historic mercury accumulation in lake sediments, northeastern United States. *Ecotoxicology*, 14, 85–99.
- Poikolainen, J., Kubin, E., Piispanen, J., & Karhu, J. (2004). Estimation of the long-range transport of mercury, cadmium, and lead to Northern Finland on the basis of moss surveys. *Arctic, Antarctic, and Alpine Research*, 36, 292–297.
- Renberg, I., Brännvall, M.-L., Bindler, R., & Empteryd, O. (2000). Atmospheric lead pollution history during four millennia (2000 B.C. to 2000 A.D. in Sweden. *Ambio*, 29, 150–156.
- Rognerud, S., Hongve, D., Fjeld, E., & Ottesen, R. T. (1999). Trace metal concentrations in lake and overbank sediments in southern Norway. *Environmental Geology*, 39, 723–732.
- Roos-Barraclough, F., Givélet, N., Shotyk, W., & Norton, S. A. (2006). A ten-thousand year record of mercury accumulation in peat from Caribou Bog, Maine, USA. *Environmental Science Technology*, 40, 3188–3194.
- Shotyk, W., Krachler, M., Martinez-Cortizas, A., Cheburkin, A. K., & Emons, H. (2002). A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12370 ^{14}C yr BP, and their variation with Holocene climate change. *Earth and Planetary Science Letters*, 199, 21–37.
- Turetsky, M. R., Manning, S. W., & Wieder, R. K. (2004). Dating recent peat deposits. *Wetlands*, 24, 324–356.
- Zielinski, G. A., Mayewski, P. A., Meeker, L. D., Whitlow, S., & Twickler, M. S. (1996). An 110,000 year record of explosive volcanism from the GISP2 (Greenland) ice core. *Quaternary Research*, 45, 109–118.

Nitrogen Saturation of Terrestrial Ecosystems: Some Recent Findings and Their Implications for Our Conceptual Framework

Bridget A. Emmett

Received: 17 July 2005 / Revised: 6 March 2006 / Accepted: 16 April 2006 / Published online: 21 February 2007
© Springer Science + Business Media B.V. 2007

Abstract The consequences of nitrogen (N) enrichment for terrestrial and freshwater ecosystems are of increasing concern in many areas due to continued or increasing high emission rates of reactive N. Within terrestrial ecosystems various conceptual frameworks and modelling approaches have been developed which have enhanced our understanding of the sequence of changes associated with increased N availability and help us predict their future impacts. Here, some recent findings are described and their implications for these conceptual frameworks and modelling approaches discussed. They are: (a) an early loss of plant species that are characteristic of low N conditions as N availability increases and a loss of species with high N retention efficiencies (so called N ‘filters’), (b) suppression of microbial immobilisation of deposited NO_3^- due to increased NH_4^+ availability in the early stages of N saturation, (c) the early onset of NO_3^- leaching due to these changes (a and b above) in both plant and microbial functioning, (d) reduced sensitivity of vegetation to N additions in areas with high historical N deposition, (e) delayed changes in soil C:N changes due to increased net primary productivity and reduced decomposition of soil organic matter. Some

suggestions of early indicators of N saturation are suggested (occurrence of mosses; $\text{NH}_4^+ : \text{NO}_3^-$ ratio in surface soils) which indicate either a shift in ecosystem function and/or structure.

Keywords diversity · eutrophication · nitrate leaching · nitrogen saturation · microbial immobilisation · soil C:N ratio · species composition

1 Introduction

Global trends of increased emissions of reactive N are of concern due to the role of oxidised and reduced forms of N in acidification and eutrophication of terrestrial and aquatic ecosystems (Bobbink et al., 1998; Fenn et al., 2003; Galloway et al., 2003; Nihlgård, 1985; Nilsson & Grennfelt, 1988; Vitousek et al., 1997). In some parts of Europe and North America reductions in the emissions of oxidised N are contributing to a stabilisation or decline in deposition but there is currently limited success in controlling emissions of reduced N. This will ensure that N will continue to have a significant environmental impact for some time to come in many regions (Galloway et al., 2003).

In 1989, Aber et al. proposed a series of hypotheses describing the long-term consequences of continuously elevated N deposition for temperate forest ecosystems and thus the progressive development of N

B. A. Emmett (✉)
Centre for Ecology and Hydrology,
Orton Building, Deiniol Rd,
Bangor LL57 2UP, UK
e-mail: bae@ceh.ac.uk

saturation (defined as N availability in excess of biotic and abiotic sinks). This conceptual model was revisited in 1998 (Aber et al., 1998) in the light of a series of N addition experiments and gradient studies in North America (Gilliam et al., 1996; Kahl et al., 1993; Magill et al., 1997; McNulty & Aber, 1993, 1996) and discussed with reference to results from European studies (e.g. Bredemeier et al., 1998; Gundersen et al., 1998b; Tietema, 1998). Other conceptual models describing the consequences of increased N deposition include those of Stoddard (1994) for freshwaters and most recently Schimel and Bennett (2004) for terrestrial N cycling in general. Current modelling approaches generally include the linkage of dynamic soil models such as with statistical or process based vegetation models (see De Vries et al., 2006 for a review). Here, some recent findings from a variety of sources are presented and their implications for these conceptual frameworks and modelling approaches discussed. Three key questions are addressed:

- (1) What is the evidence for N-driven changes in biodiversity and what is the dose response function?
- (2) How will vegetation change affect N retention?
- (3) What are the underlying processes which 'trigger' the onset of NO_3^- leaching and are there useful indicators of current N status of ecosystems at this critical point?

2 (1) What is the Evidence for N-driven Changes in Biodiversity and What is the Dose Response Function?

Various reviews or syntheses for specific regions are available which summarise the evidence available for the long term effects of N deposition on biodiversity including Bobbink et al. (1998) and Fenn et al. (2003). Mechanisms for changes in species composition including species loss are complex and have been discussed by Bobbink et al. (1998), Smart et al. (2005), Suding et al. (2005) and Pennings et al. (2005). They include increased competition due to increased production and increased biotic and abiotic stresses. Species of low abundance appear to be particularly at risk (Suding et al., 2005). Sources of information used in these reviews or analyses include; (a) monitoring programmes; (b) one-off

spatial surveys where a space-for-time substitution is accepted and (c) N addition/reduction experiments. As there are limitations to all three approaches, it is valuable to examine the findings for one region and compare their conclusions to see if there are inconsistencies which can help inform our understanding of the sequence and timing of changes in biodiversity associated with increased N deposition. Within the UK, findings from two long term monitoring programmes, one spatial survey and several long term N manipulation experiments have recently been published which enable this comparison to be done which reveal both similarities and discrepancies in their findings.

Results from the two long term monitoring programmes both suggest that there have been wide-ranging changes in species occurrence in the UK during the latter half of 20th century associated with increased N availability: (a) The New Plant Atlas of the UK (Preston et al., 2002) provides evidence for a decline in the frequency of occurrence of plant species characteristic of low nutrient availability between 1930–1969 and 1987–1999 and an increase in the geographic range of species associated with high nutrient availability (Fig. 1a). (b) A survey of UK habitats using a stratified sampling approach called the Countryside Survey (<http://www.cs2000.org.uk>) has reported on results from repeated surveys of higher plant species data from permanent quadrats from 1978–1990 and 1990–1998. Results again suggest a shift towards plant species associated with high nutrient availability particularly in low nutrient habitats such as heathland and infertile grasslands (Haines-Young et al., 2003; Smart et al., 2003) (Fig. 1b).

Both studies use Ellenberg nutrient scores which indicate the nutrient requirement of individual higher plant species and can be used to highlight the importance of an environmental factor in defining the vegetation composition (Ellenberg et al., 1991). Whilst the Ellenberg nutrient availability index does not distinguish N from other nutrient elements, N is often the most limiting element in many terrestrial ecosystems and changes in inputs of other nutrients from atmospheric sources are unlikely. Increases in Ellenberg scores are thus often used to indicate enrichment from atmospheric N deposition in the absence of direct fertilizer inputs although attributing causal drivers is always problematic.

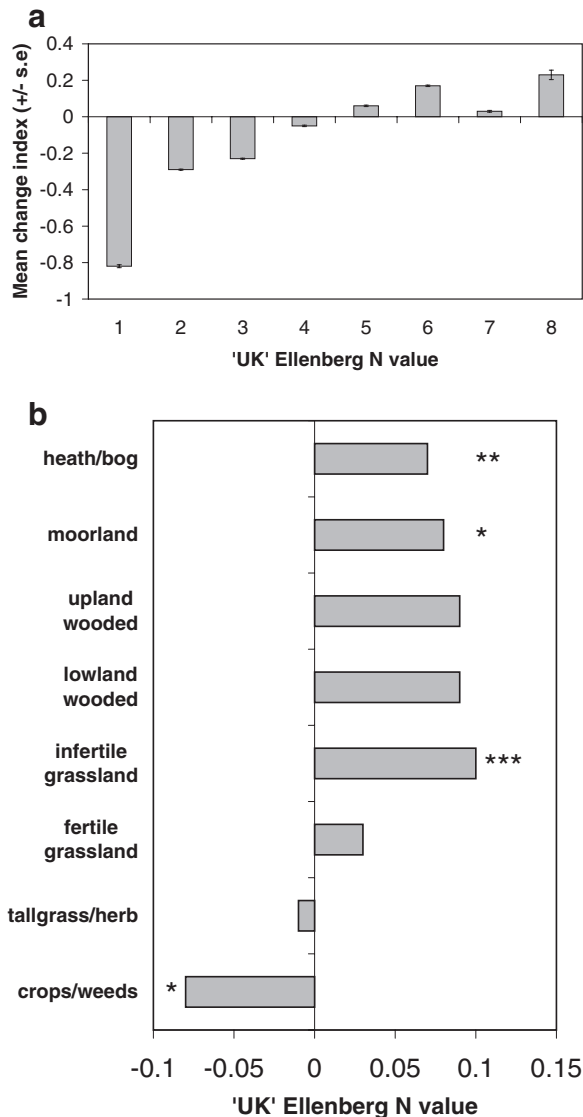


Fig. 1 Changes in vegetation composition in the UK according to their UK Ellenberg Nutrient (N) values (Hill et al., 1999). A low value is associated with low N fertility and high value with high N fertility: **a** The mean change index for occurrence of plant species classified according to their UK Ellenberg (N) values between 1930–1969 and 1987–1999 as reported in the New Atlas of the British and Irish Flora (Drawn from data presented in Preston et al., 2002). Standard errors are indicated. **b** The change in UK Ellenberg N score for different habitats between 1990 and 1998 taken from the most recent UK Countryside Survey (redrawn from Haines-Young et al., 2003). Statistically significant changes are marked as * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

The results from these two monitoring programmes appear consistent with evidence from a spatial survey recently undertaken in acid grassland by Stevens et al.

(2004) in the UK (Fig. 2). This habitat was identified in the Countryside Survey as one in which a shift towards species associated with high nutrient availability was particularly marked. Results from the spatial survey, where the space for time substitution was accepted, indicated a decline in species richness as N inputs increased with the largest decline observed between 10 and 15 kgN/ha/yr indicating not only a change in species composition but also a loss in species richness *per se*. Relationships to other variables such as climate, soil characteristics and grazing pressure were not as strong.

The conclusions from this spatial survey and the two long term monitoring programmes can be tested against data from several long term N addition experiments in nutrient-poor grassland and heathlands in the UK (<http://www.bangor.ceh.ac.uk/terrestrial-umbrella/>). In contrast to expectations, no loss of higher plant species have been recorded (Power et al., 1998; Carroll et al., 1999, 2003; Emmett et al., 2004) although major changes in bryophytes were noted (Carroll et al., 2000). One explanation for the relative insensitivity of the higher plants in these experimental studies could be a reduced sensitivity in ecosystems which have had sustained elevated N deposition for many decades (i.e. >10 kgN/ha/yr) due to previous loss of sensitive plant species whether due to their low abundance or functional traits. One experimental approach to test the possibility of both past species change and reduced sensitivity in systems which

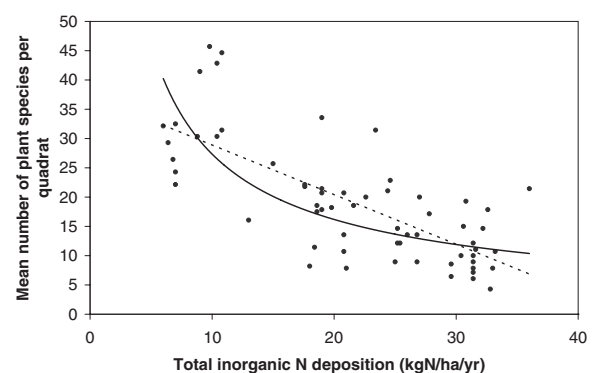


Fig. 2 The number of acid grassland species plotted against and N deposition redrawn from Stevens et al. (2004). The original linear regression line ($r^2=0.55$) is shown (dashed line) and a new power function (solid line) which explains less of the variance ($r^2=0.49$) but mirrors relationships described elsewhere (e.g. Haddad et al., 2000) and results from field experiments in the UK (see text)

have experienced chronic N deposition is to compare results from N addition and reduction at one location. N reduction is unfortunately expensive to carry out in the field although very informative about impacts of ambient N deposition on vegetation composition and tree growth (e.g. Bobbink et al., 1998). A simpler approach on acid grassland cores was recently carried out by Jones (2005) using experimental misting facilities. Intact blocks of vegetation and soil were removed from an acid grassland receiving 20 kgN/ha/yr and exposed to either increased N inputs (>20 kgN/ha/yr) or reduced N inputs (<20 kgN/ha/yr) using the experimental misting facilities. The results indicated some species were highly sensitivity to reductions in N inputs providing evidence both for current 'damage' to this system and potential for recovery (Fig. 3). A range of responses was observed which suggested different critical limits for different species. The limited response by higher plants to N additions was confirmed in a N addition field experiment *in situ* which had resulted in only small shifts in species dominance and no loss of plant species confirming this system was relatively insensitive to N (Emmett et al., 2004). When comparing these results to the relationship reported from the spatial survey for the same habitat across the UK, it can be seen that if a power function is used to describe the data presented by Stevens et al. (2004) rather than the linear relationship the authors proposed (Fig. 2), this emphasises the possibility of a reduced rate of species loss at site receiving >20 kgN/ha/yr which

follows findings from the experimental studies and relationships reported elsewhere (e.g. Haddad et al., 2000).

The comparison of results from three sources confirms the need with all experimental and survey work to consider the possibility of past conditioning which may have already led to loss of rare or sensitive species and a reduction in species richness. It also suggests that species change or loss may be quite sensitive to N availability and occurs early in the sequence of N saturation.

3 (2) How Will Changes in Vegetation Composition Affect N Retention?

A large number of surface water quality monitoring programmes have been examined for evidence of increased N leaching. For example, an analysis of regional trends in surface-water chemistry indicated small but positive increases in NO_3^- concentrations in the 1980s in parts of Europe, the Nordic countries and part of NE USA (Stoddard et al., 1999). This positive trend disappeared in the 1990s possibly as a result of emission controls which helped to stabilise or reduce deposition of oxidised N in these regions. However, other long term monitoring studies of specific sites or regions have not identified any responses to changes in N deposition due to the complexity of drivers which can affect N cycling and thus NO_3^- leaching (e.g. Cooper, 2005; Goodale et al., 2003). Spatial surveys also show a high degree of variability in the relationship between N deposition and NO_3^- leaching (e.g. Aber et al., 2003; Dise & Wright, 1995) as do N addition and reduction experiments (e.g. Aber et al., 1989; Bredemeier et al., 1998; Emmett et al., 1998a). This variability has been linked to a range of confounding factors which determine the N status of a site and thus the sensitivity of an ecosystem to ambient or experimentally changed N deposition. Most studies point to the soil N store as the dominant sink for deposited N in the short and long term (e.g. Nadelhoffer et al., 1999a, 1999b). Thus, parameters which are linked to the retention capacity of the soil are generally identified as the most important predictors of the speed and magnitude of change in NO_3^- leaching in response to elevated N deposition. Put very simply, the magnitude of NO_3^- leaching from sites appears to be

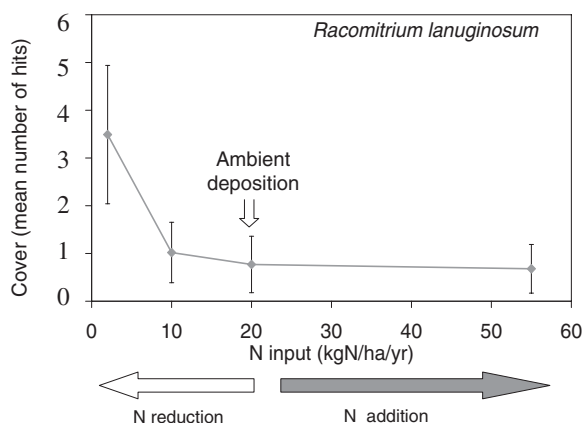


Fig. 3 Change in cover as detected by pin pointing (hits) of the moss *Racomitrium lanuginosum* to both N additions (>20 kgN/ha/yr) and N reductions (<20 kgN/ha/yr) in acid grassland mesocosms in an experimental misting facility which excluded ambient N deposition (redrawn from Jones, 2005). Standard errors are shown

best predicted by the overall size of the soil C pool and/or contact time, the amount of N already associated with the soil C and the annual N deposition rate (see Aber et al., 2003; Dise & Wright, 1995; Evans et al., 2006; Fenn et al., 1998; Gundersen et al., 1998a; Macdonald et al., 2002; Matzner & Grosholz, 1998; Williard et al., 1997).

Although the soil is the dominant sink for N, the vegetation clearly has a critical role in retention of N both directly through plant uptake and indirectly through provision of the C for heterotrophic uptake in the soil (see Aber et al., 1998 for possible mechanisms). In forest systems, the direct role of plant uptake is generally only observed in the soil or streamwater NO_3^- signal when comparing stands with large differences in net accumulation rates such as even-aged, monoculture stands which are aggrading (e.g. Emmett et al., 1993). In more diverse forest systems, relationships between NO_3^- leaching and stand age are not observed (e.g. Goodale et al., 2003) although species differences have been noted in some forest systems (e.g. Lovett et al., 2002). This leads to the possibility of species change as N saturation progresses directly affecting the N retention capacity of a system. This has been demonstrated in one study by Curtis et al. (2005) where a ^{15}N tracer approach was used to quantify the retention of applied N in different ecosystem components within four acid grassland- and ericoid shrub-dominated catchments across a UK N deposition gradient. The amount of ^{15}N not recovered in plant and soil pools after one year of application was found to be directly proportional to the NO_3^- leaching losses at the different sites. The ^{15}N not recovered (which was assumed to have been leached from the system) was closely correlated to a reduction in the ^{15}N recovered in the bryophyte and lichen pools which were found to be important components of total biomass and have the highest N retention efficiencies (i.e. N uptake per gram biomass) (Fig. 4). Retention in the soil and higher plant pools remained the same across the deposition gradient. These results suggested that bryophytes and lichens appeared to be an important sink for deposited N by reducing the amount of inorganic-N available to both higher plants and soil microbes. The importance of a moss 'N filter' has previously been described for raised bogs in controlling invasion of vascular plant and C storage (Lamers et al., 2000) but the study by Curtis et al. also suggest this also may be important

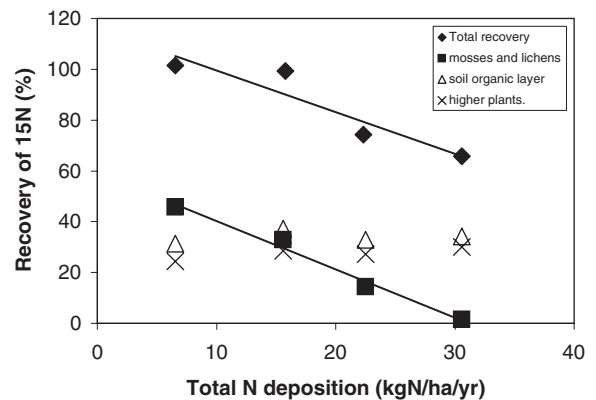


Fig. 4 Recovery of ^{15}N applied over one year to experimental plots in acid grassland and heathlands across a UK N deposition gradient. *Solid lines* through total recovery and mosses and lichen symbols are *linear regression lines*. Redrawn from Curtis et al. (2005)

in grassland and heathland systems in controlling N leaching. As high N inputs can cause physiological damage to lower plants and also a reduction in biomass (e.g. Press et al., 1986), an important 'N filter' may be lost when N inputs increase thereby contributing to the early onset of NO_3^- leaching. Assessment in terms of biomass and/or physiological health of bryophytes and lichens may provide a useful indicator of early stages of N saturation and onset of NO_3^- leaching for some habitats.

When considering the importance of changes in plant composition for N retention as N saturation progresses, the main mechanism for vegetation-driven changes in N cycling is usually considered as alteration of litter quality which affect the rates of litter decomposition and associated organic matter quality. A shift to species with higher litter quality will lead to increased rates of decomposition and higher N availability. However, litter quality also affects the response of organic matter decomposition to N additions. For example, Waldrop et al. (2004) observed that N additions in a forest ecosystem with low litter quality (i.e. highly lignified) increased soil C storage due to a reduction in phenol oxidase activity whilst a forest with high litter quality lost soil C. In other studies, N additions were observed to lower the activity of lignolytic enzymes including phenol oxidase (e.g. Carreiro et al., 2000) and mineralisation of soil organic matter (e.g. Hagedorn et al., 2003) although again results depend on litter quality and soil type. Litter decomposition studies have also highlighted the importance of litter quality in determining the effect

of N additions on decomposition rates and thus C and N mineralization rates (Berg & Meentemeyer, 2002). Whilst these results suggest there could be a positive feedback of N deposition on C and N storage in some nutrient-poor systems, the opposite may be true in high litter quality systems suggesting that current differences in C and N retention between nutrient rich and poor systems may be reinforced by continuing N deposition. However, these studies only reflect the decomposition dynamics of current soil organic matter. The net effect of N deposition on C and N retention at the ecosystem scale will be dependent on a range of factors including the response of net primary production, changes in litter quality associated with species change, and shifts in functional-traits of species present (e.g. N filters or fixers).

4 (3) What are the Underlying Processes which ‘Trigger’ the Onset of NO_3^- Leaching and are there Useful Indicators of Current N Status of Ecosystems at this Critical Point?

The soil C:N ratio has been used to predict the N retention capacity of the soil and thus the potential for NO_3^- leaching for forest systems and has been observed to be related to NO_3^- leaching, nitrification and denitrification rates in a similar way in several different regions (Adams et al., 2004). It is thought to be an indicator of the balance between gross mineralisation and immobilisation of N and therefore the amount of inorganic N which is available for uptake and leaching and is an important parameter in many soil chemistry models. However, some of the experimental data suggests that significant changes in NO_3^- leaching can occur without changes in soil C:N ratio. For example, in one N addition study at Gårdsjön, Sweden, 50 kgN/ha/yr has been applied to a spruce forest since 1991 (Moldan et al., 2006). This has resulted in increased NO_3^- leaching from <1 to 10% of inputs in 2003 although the soil organic horizon C:N ratio has not changed during this time probably due to N-induced increases in plant production. Likewise for biodiversity, soil C:N has been found to be a relatively poor predictor of the increased N availability which drives changes in species composition (e.g. Ertsen et al., 1998; Stevens et al., 2004). Reasons could include shifts in the form of N utilised by plants and lags in changes in bulk soil

C:N as N deposition increases. Schimel and Bennett (2004) recently highlighted the likely importance of competition between microbes and plants at the microsite scale as N availability increases. These processes would not be reflected in bulk soil C:N but could have significant impacts on the form and amount of N available for leaching. In addition, an important shift in the early stages of N enrichment is the change in the form of N used by microbes and plants from organic-N to inorganic-N which would not be reflected in the soil C:N. For plants, the shift may be linked to high cellular NH_4^+ concentrations which inhibit amino-acid uptake (Persson & Näsholm, 2002). As N availability increases still further, high rhizosphere NH_4^+ concentrations and high internal amino acid concentrations can suppress NO_3^- uptake by trees (Gessler et al., 2004) which could contribute to the risk of NO_3^- being leached from the system.

A similar switch in the form of N used is observed for microbes which can have a high potential for NO_3^- immobilisation (Davidson et al., 1991; Hart et al., 1994; Stark & Hart, 1997) and be an important sink for deposited NO_3^- in some forest systems (Zak et al., 2004; Davidson et al., 1992; Zogg et al., 2000). However, increased NH_4^+ availability causes disruption of NO_3^- uptake and suppression of the synthesis and activity of NO_3^- assimilatory enzymes thus reducing the consumption of NO_3^- . This has been described using laboratory microorganisms by Van't Riet et al. (1968) and Betlach et al. (1981), and in isolates from soil by Rice & Tiedje (1989). More recently, the ecological significance of this feedback in forest soils was tested in a study in a clearcut forest in British Columbia by Bradley (2001). The relative effects of additions of NH_4^+ and glucose on NO_3^- production and consumption were tested and NH_4^+ additions found to have little effect on gross NO_3^- production but strongly reduced gross immobilisation of NO_3^- (Fig. 5). No effect of glucose was observed on either NO_3^- production or immobilisation. These findings together with results from various field studies suggest that the suppression of immobilisation of deposited NO_3^- rather than stimulation of NO_3^- production is the dominant process determining the onset of NO_3^- leaching. These field studies include; (a) N addition studies where NO_3^- leaching losses were found to increase in response to NO_3^- additions rather than total inorganic-N inputs (Emmett et al., 1998b), (b) ^{15}N tracer experiments where NO_3^- leached is

shown to be predominantly the NO_3^- applied during the same year (Providoli et al., 2005; Tietema et al., 1998), and (c) roof experiments where NO_3^- leaching is quickly and significantly reduced when N-inputs are removed indicating an external source of leached N (Bredemeier et al., 1998). Some natural abundance isotopic studies have indicated a microbial source of NO_3^- in soil and streamwater which conflicts with this finding (Pardo et al., 2004) as do some tracer studies (Nadelhoffer et al., 1999a, 1999b). Reasons for these conflicting findings are not well understood at present. One explanation may be a greater contribution from deposited NO_3^- in high flow conditions which would dominate export fluxes.

Do these findings help in the search for simple and practical indicators of the N status of ecosystems and in particular the risk of NO_3^- leaching and biodiversity change? Shifts in the balance between gross and net rates of soil N transformations have been proposed at various times as indicators or changes in N availability e.g. a large ratio of gross nitrification/gross immobilisation (Goulding et al., 1998) or a decreasing ratio of gross/net mineralization and nitrification (Aber, 1992). Whilst ^{15}N pool dilution studies are invaluable at enabling actual rates of inorganic-N production to be quantified rather than net rates, they are costly and time consuming and thus unlikely to be suitable as indicators. One simpler and cheaper indicator of both a shift in microbial functioning (in particular the suppression of microbial immobilisation of NO_3^-) and the N form available to plants may be the exchangeable $\text{NH}_4^+:\text{NO}_3^-$ ratio in surface soils standardised for organic matter content for different habitats. In a

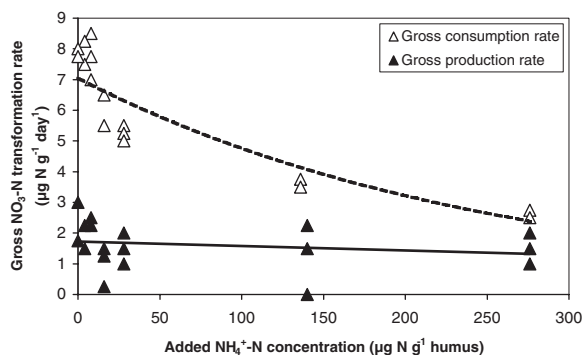


Fig. 5 The response of gross NO_3^- production and consumption to NH_4^+ additions in a forest soil (redrawn from Bradley, 2001)

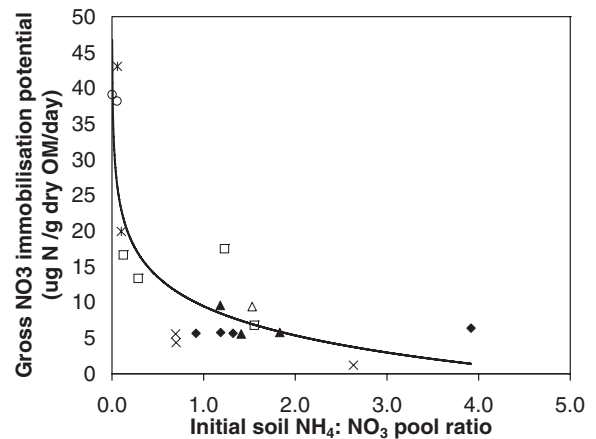


Fig. 6 The relationship between initial extractable $\text{NH}_4^+:\text{NO}_3^-$ and gross NO_3^- immobilisation quantified using the ^{15}N pool dilution approach from both control and N addition plots in grassland and ericoid-shrub systems. Different symbols indicate different sites (Redrawn from Hughes et al., 2004)

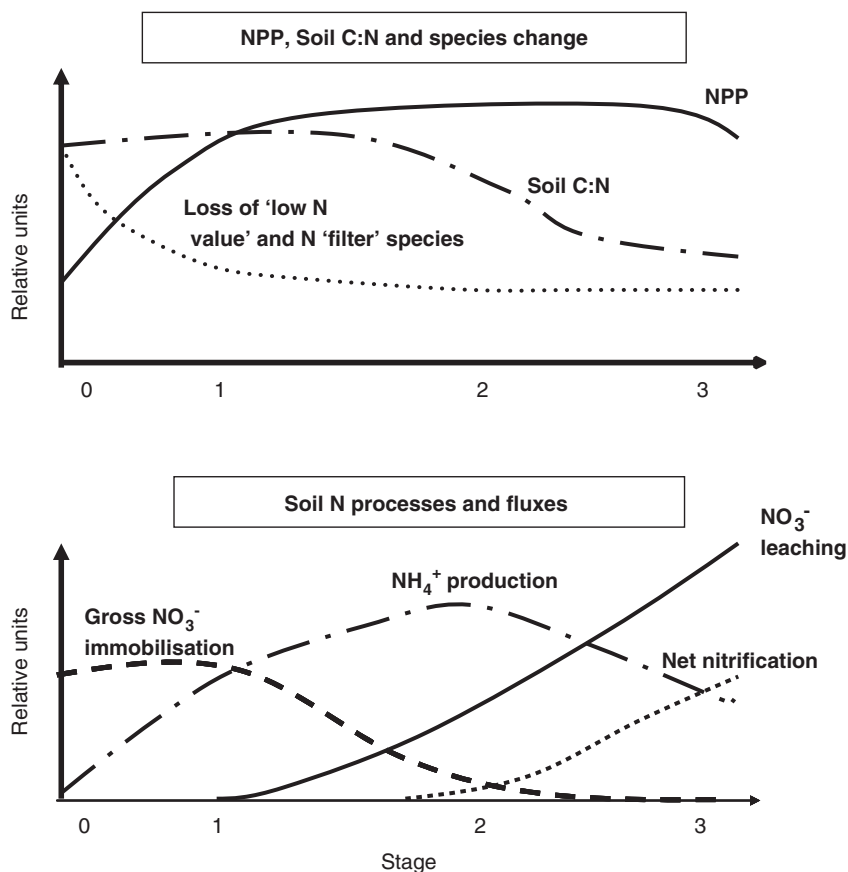
recent study in acid grassland and ericoid-shrubland systems in the UK, gross microbial immobilisation of NO_3^- measured using the ^{15}N pool dilution approach was found to be most strongly related to the initial extractable $\text{NH}_4^+:\text{NO}_3^-$ ratio rather than rates of N addition (Fig. 6) (Hughes et al., 2004). However, this is likely only to be useful during the initial stages of N saturation enrichment before bulk soil C:N changes are detected and not in soils which have been heavily polluted with ammonia inputs.

5 Conclusions

The findings from the various studies described here can be placed according to the ‘Stages’ of N saturation described by Aber et al. (1989, 1998) to highlight their timing and interrelationship (Fig. 7):

- Early loss of plant species associated with low fertility as N availability increases and loss of species which act as ‘N filters’
- Increased NH_4^+ concentrations and an associated suppression of microbial immobilisation deposited NO_3^- as enrichment increases
- The early onset of NO_3^- leaching due to (a) and (b) described above
- Reduced sensitivity of vegetation composition as N availability increases due to past loss of most sensitive species

Fig. 7 Proposed timing of different ecosystem components as N saturation progresses through various 'Stages' initially described by Aber et al. (1989, 1998). Relative changes are shown for; net primary productivity (NPP), soil C:N, occurrence of plant species associated with low N availability or which act as 'N filters' (see text for explanation), gross microbial nitrate immobilisation, ammonium production, net nitrification and nitrate leaching



- (e) increased primary production and reduced decomposition of soil organic matter which maintain soil C:N ratios despite increased N availability

Acknowledgements The UK Department of the Environment, Food and Rural Affairs and the Natural Environment Research Council provided the funding for many of the UK studies reported here and the time for this synthesis. My thanks to the Acid Rain 2005 Organising Committee for giving me the opportunity to share these ideas and to the many colleagues and two referees for their helpful comments.

References

- Aber, J. D. (1992). Nitrogen cycling and nitrogen saturation in temperate forest ecosystems. *Trends in Ecology & Evolution*, 7, 220–224.
- Aber, J. D., Goodale, C., Ollinger, S. V., Smith M., Magill, A., & Martin, M. E., et al. (2003). Is nitrogen deposition altering the nitrogen status of Northeastern forests? *Bioscience*, 53, 375–389.
- Aber, J. D., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., & Kamakea, M., et al. (1998). Nitrogen saturation in temperate forest ecosystems: Hypotheses revisited. *Bioscience*, 48, 921–934.
- Aber, J. D., Nadelhoffer, K. J., Steudler, P., & Melillo, J. M. (1989). Nitrogen saturation in northern forest ecosystems. *Bioscience*, 39, 378–386.
- Adams, M., Ineson, P., Binkley, D., Cadisch, G., Scholes, M., Hicks, K., & Tokuchi, N. (2004). Soil functional responses to excess nitrogen inputs at global scale. *Ambio*, 33, 530–536.
- Berg, B., & Meentemeyer, V. (2002). Litter quality in a north European transect versus carbon storage potential. *Plant and Soil*, 242, 83–92.
- Betlach, M. R., Tiedje, J. M., & Firestone, R. B. (1981). Assimilatory nitrate uptake in *Pseudomonas fluorescens* studied using Nitrogen-13. *Archives of Microbiology*, 129, 135–140.
- Bobbink, R., Hornung, M., & Roelofs, J. G. M. (1998). The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. *Journal of Ecology*, 86, 717–738.
- Bradley, R. L. (2001). An alternative explanation for the post-disturbance NO_3^- flush in some forest ecosystems. *Ecology Letters*, 4, 412–416.

- Bredemeier, M., Blanck, K., Xu, Y. J., Tietema, A., Boxman, A. W., & Emmett, B. A., et al. (1998). Input-output budgets at the NITREX sites. *Forest Ecology and Management*, 101, 57–64.
- Carreiro, M. M., Sinsabaugh, R. L., Repert, D. A., & Parkhurst, D. F. (2000). Microbial enzyme shifts explain litter decay responses to simulated nitrogen deposition. *Ecology*, 81, 2359–2365.
- Carroll, J. A., Caporn, S. J. M., Cawley, L., Read, D. J., & Lee, J. A. (1999). The effect of increased deposition of atmospheric nitrogen on *Calluna vulgaris* in upland Britain. *New Phytologist*, 141, 423–431.
- Carroll, J. A., Caporn, S. J. M., Johnson, D., Morecroft, M. D., & Lee, J. A. (2003). Interactions between plant growth, vegetation structure and soil processes in semi-natural acidic and calcareous grasslands receiving long-term inputs of simulated pollutant nitrogen deposition. *Environmental Pollution*, 121, 363–376.
- Carroll, J. A., Johnson, D., Morecroft, M., Taylor, A., Caporn, S. J. M., & Lee, J. A. (2000). The effect of long-term nitrogen additions on the bryophyte cover of upland acidic grasslands. *Journal of Bryology*, 22, 83–89.
- Cooper, D. M. (2005). Evidence of sulphur and nitrogen deposition signals at the United Kingdom acid waters monitoring network sites. *Environmental Pollution*, 137, 41–54.
- Curtis, C. J., Emmett, B. A., Grant, H., Kernan, M., Reynolds, B., & Shilland, E. (2005). Nitrogen saturation in UK moorlands: The critical role of bryophytes and lichens in determining retention of atmospheric N deposition. *Journal of Applied Ecology*, 42, 507–517.
- Davidson, E. A., Hart, S. C., & Firestone, M. K. (1992). Internal cycling of nitrate in soils of a mature coniferous forest. *Ecology*, 73, 1148–1156.
- Davidson, E. A., Hart, S. C., Shanks, C. A., & Firestone, M. K. (1991). Measuring gross nitrogen mineralization, immobilization and nitrification by ^{15}N isotopic pool dilution in intact soil cores. *Journal of Soil Science*, 42, 335–349.
- De Vries, W., Kros, H., Reinds, G. J., Wamelink, W., Van Dobben, H., & Bobbink, R., et al. (2006). *Development in modelling critical nitrogen loads for terrestrial ecosystems in Europe*. Alterra, CCE report 2006. pp. 186 (in preparation).
- Dise, N., & Wright R. F. (1995). Nitrogen leaching in European forests in relation to nitrogen deposition. *Forest Ecology and Management*, 71, 153–162.
- Ellenberg, H., Weber, H. E., Düll, R., Wirth, W., Werner, W., & Paulissen, D. (1991). Zeigerwerte von Pflanzen in Mitteleuropa. *Scripta Geobotanica*, 18, 1–248.
- Emmett, B. A., Boxman, D., Bredemeier, M., Gundersen, P., Kjonaas, O. J., & Moldan, F., et al. (1998a). Predicting the effects of atmospheric nitrogen deposition in conifer stands: Evidence from the NITREX ecosystem-scale experiments. *Ecosystems*, 1, 352–360.
- Emmett, B. A., Jones, M. L. M., Jones, H., Wildig, J., Williams, B., & Davey, M., et al. (2004). *Grazing/nitrogen deposition interactions in upland acid moorland. Contract report to Countryside Council for Wales (Contract no. FV-73-03-89B) and the National Assembly for Wales (Contract No. 182-2002)*. pp. 96.
- Emmett, B. A., Reynolds, B., Silgram, M., Sparks, T. H., & Woods, C. (1998b). The consequences of chronic nitrogen additions on N cycling and soilwater chemistry in a N saturated Sitka spruce stand, North Wales. *Forest Ecology and Management*, 101, 165–175.
- Emmett, B. A., Reynolds, B., Stevens, P. A., Norris, D. A., Hughes, H., & Görres, J., et al. (1993). Nitrate leaching from afforested Welsh catchments – Interactions between stand age and nitrogen deposition. *Ambio*, 22, 386–394.
- Ertsen, A. C. D., Alkemade, J. R. M., & Wassen, M. J. (1998). Calibrating Ellenberg indicator values for moisture, acidity, nutrient availability and salinity in the Netherlands. *Plant Ecology*, 135, 113–124.
- Evans, C. D., Reynolds, B., Jenkins, A., Helliwell, R., Curtis, C. J., & Goodale, C. L., et al. (2006). Evidence that soil carbon pool determines susceptibility of semi-natural ecosystems to elevated nitrogen leaching. *Ecosystems*, 9, 453–462.
- Fenn, M. E., Baron, J. S., Allen, E. B., Rueth, H. M., Nydick, K. R., & Geiser, L., et al. (2003). Ecological effects of nitrogen deposition in the Western United States. *Bioscience*, 53, 404–420.
- Fenn, M. E., Poth, M. A., Aber, J. D., Baron, J. S., Bormann, B. T., & Johnson, D. W., et al. (1998). Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses and management strategies. *Ecological Applications*, 8, 706–733.
- Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., & Cowling, E. B., et al. (2003). The nitrogen cascade. *Bioscience*, 53, 341–356.
- Gessler, A., Kopriva, S., & Rennenberg, H. (2004). Regulation of nitrate uptake at the whole-tree level: Interaction between nitrogen compounds, cytokinins and carbon metabolism. *Tree Physiology*, 24, 1313–1321.
- Gilliam, F. S., Adams, M. B., & Yurich, B. M. (1996). Ecosystem nutrient responses to chronic nitrogen inputs at Fernow Experimental Forest, West Virginia. *Canadian Journal of Forest Research*, 26, 196–205.
- Goodale, C. L., Aber, J. D., & Vitousek, P. M. (2003). An unexpected nitrate decline in New Hampshire streams. *Ecosystems*, 6, 75–86.
- Goulding, K. W. T., Bailey, N. J., Bradbury, N. J., Hargreaves, P., Howe, M., & Murphy, D. V., et al. (1998). Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes. *New Phytologist*, 139, 49–58.
- Gundersen, P., Callensen, I., & de Vries, W. (1998a). Nitrogen leaching in forest ecosystems is related to forest floor C/N ratios. *Environmental Pollution*, 102, 403–407.
- Gundersen, P., Emmett, B. A., Kjonaas, O. J., Koopmans, C. J., & Tietema, A. (1998b). Impact of nitrogen deposition on nitrogen cycling in forests: A synthesis of NITREX data. *Forest Ecology and Management*, 101, 37–56.
- Haddad, N. M., Haarstad, J., & Tilman, D. (2000). The effects of long-term nitrogen loading on grassland insect communities. *Oecologia*, 124, 73–84.
- Hagedorn, F., Spinnler, D., & Siegwolf, R. (2003). Increased N deposition retards mineralization of old soil organic matter. *Soil Biology and Biochemistry*, 35, 1683–1692.
- Haines-Young, R., Barr, C. J., Firbank, L. G., Furse, M., Howard, D. C., & McGowan, G., et al. (2003). Changing landscapes, habitats and vegetation diversity across Great Britain. *Journal of Environmental Management*, 67, 267–281.

- Hart, S. C., Nason, G. E., Myrold, D. D., & Perry, D. A. (1994). Dynamics of gross nitrogen transformations in an old-growth forest: The carbon connection. *Ecology*, 75, 880–891.
- Hill, M. O., Mountford, J. O., Roy, D. B., & Bunce, R. G. H. (1999). *Ellenberg's indicator values for British plants*. ECOFACT Volume II, Technical Annex. Huntingdon, UK: ITE Monkswood.
- Hughes, S., Grant, H., Ostle, N., Emmett, B. A., & UKREATE. (2004). The controls on immobilisation of ammonium and nitrate and the link to the onset of N saturation. In B. A. Emmett & G. McShane (Eds.), *Terrestrial Umbrella Final Report May 2004* (pp. 321–329). NERC-DEFRA Terrestrial Umbrella Contract Number EPG 1/3/186.
- Jones, M. L. M. (2005). *Nitrogen deposition in upland grasslands: Critical loads, management and recovery*. PhD Thesis, University of Sheffield, UK.
- Kahl, J. S., Norton, S. A., Fernandez, I. J., Nadelhoffer, K. J., Driscoll, C. T. Y., & Aber, J. D. (1993). Experimental inducement of nitrogen saturation at the watershed scale. *Environmental Science & Technology*, 27, 565–568.
- Lamers, L. P. M., Bobbink, R., & Roelofs, J. G. M. (2000). Natural nitrogen filter fails in polluted raised bogs. *Global Change Biology*, 6, 583–586.
- Lovett, G. M., Weathers, K. C., & Arthur, M. A. (2002). Control of nitrogen loss from forests by soil carbon: Nitrogen ratio and tree species composition. *Ecosystems*, 5, 712–718.
- Macdonald, J. A., Dise, N. B., Matzner, E., Armbruster, M., Gundersen, P., & Forsius, M. (2002). Nitrogen inputs together with nitrogen enrichment predict nitrate leaching in European forests. *Global Change Biology*, 8, 1028–1033.
- Magill, A. H., Aber, J. D., Hendricks, J. J., Bowden, R. D., Melillo, J. M., & Steudler, P. (1997). Biogeochemical response of forest ecosystems to simulated chronic nitrogen deposition. *Ecological Applications*, 7, 402–415.
- Matzner, E., & Grosholz, C. (1998). Beziehung zwischen NO_3^- Austrägen, C/N-Verhältnissen ser Auflage und N-Einträgen in Fichtenwald (*Picea abies* Karst)-Ökosystemen Mitteleuropas. *Forstwissenschaftliches Centralblatt*, 116, 39–44.
- McNulty, S. G., & Aber, J. D. (1993). Effects of chronic nitrogen additions on nitrogen cycling in a high-elevation spruce-fir stand across New England. *Biogeochemistry*, 14, 13–29.
- McNulty, S., & Aber, J. D. (1996). Nitrogen saturation in a high elevation New England spruce-fir stand. *Forest Ecology and Management*, 84, 109–121.
- Moldan, F., Kjonaas, O. J., Stuanes, A. O., & Wright, R. F. (2006). Increased nitrogen in runoff and soil following thirteen years of experimentally increased nitrogen deposition to a coniferous-forested catchment at Gårdsjön, Sweden. *Environmental Pollution* 144(2):610–620.
- Nadelhoffer, K., Downs, M., Fry, B., Magill, A., & Aber, J. (1999a). Controls on N retention and exports in a forested watershed. *Environmental Monitoring and Assessment*, 55, 187–210.
- Nadelhoffer, K. J., Emmett, B. A., Gundersen, P., Kjonaas, O. J., Koopmans, C. J., & Schleggi, P., et al. (1999b). Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature*, 398, 145–148.
- Nihlgård, B. (1985). The ammonium hypothesis: An additional explanation to the forest dieback in Europe. *Ambio*, 14, 2–8.
- Nilsson, J., & Grennfelt, P. (Eds.) (1988). *Critical Loads for Sulphur and Nitrogen*. Report of the Skokloster Workshop. Miljörapport 15. Nordic Council of Ministers, Copenhagen.
- Pardo, L. H., Kendall, C., Pett-Ridge, J., & Chang, C. C. Y. (2004). Evaluating the source of streamwater nitrate using delta N-15 and delta O-18 in nitrate in two watersheds in New Hampshire, USA. *Hydrological Procedure*, 18, 2699–2712.
- Pennings, S. C., Clark, C. M., Cleland, E. E., Collins, S. L., Gough, L., & Gross, K. L., et al. (2005). Do individual plant species show predictable responses to nitrogen addition across multiple experiments. *Oikos*, 110, 547–555.
- Persson, J., & Näsholm, T. (2002). Regulation of amino acid uptake in conifers by exogenous and endogenous nitrogen. *Planta*, 215, 639–644.
- Power, S. A., Ashmore, M. R., & Cousins, D. A. (1998). Impacts and fate of experimentally enhanced nitrogen deposition on a British lowland heath. *Environmental Pollution*, 102(Suppl. 1), 27–34.
- Press, M. C., Woodin, S. J., & Lee, J. A. (1986). The potential importance of increased nitrogen supply to the growth of the ombrotrophic Sphagnum species. *New Phytologist*, 138, 45–55.
- Preston, C. D., Pearman, D. A., & Dines, T. D. (2002). *New Plant Atlas of the British and Irish Flora* (p. 42). New York: Oxford University Press.
- Providoli, I., Bugmann, H., Siegwolf, R., Buchmann, N., & Schleggi, P. (2005). Flow of deposited inorganic N in two Gleysol-dominated mountain catchments traced with $^{15}\text{NO}_3^-$ and $^{15}\text{NH}_4^+$. *Biogeochemistry*, 76, 453–475.
- Rice, C. W., & Tiedje, J. M. (1989). Regulation of nitrate assimilation by ammonium in soils and in isolated soil microorganisms. *Soil Biology & Biochemistry*, 21, 597–602.
- Schimel, J. P., & Bennett, J. (2004). Nitrogen mineralization: Challenges of changing paradigm. *Ecology*, 85, 591–602.
- Smart, S. M., Bunce, R. G. H., Marrs, R. H., LeDuc, M., Firbank, L. G., & Maskell, L. C., et al. (2005). Large-scale changes in the abundance of common plant species across Britain between 1978, 1990 and 1998 as a consequence of human activity: Tests of hypothesised changes in trait representation. *Biological Conservation*, 124, 355–371.
- Smart, S. M., Robertson, J. C., Shiel, E. J., & van de Poll, H. M. (2003). Locating eutrophication effects across Britain vegetation between 1990 and 1998. *Global Change Biology*, 9, 1763–1774.
- Stark, J. M., & Hart, S. C. (1997). High rates of nitrification and nitrate turnover in undisturbed coniferous forests. *Nature*, 385, 61–64.
- Stevens, C. J., Dise, N. B., Mountford, J. O., & Gowing, D. J. (2004). Impact of nitrogen deposition on the species richness of grasslands. *Science*, 303, 1876–1879.
- Stoddard, J. L. (1994). Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. In L. A. Baker (Ed.), *Environmental chemistry of lakes and reservoirs* (pp. 223–284). Wahsington, DC: American Chemical Society.
- Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., & Driscoll, C. T., et al. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature*, 401, 575–578.

- Suding, K. N., Collins, S. L., Gough, L., Clark, C., Cleland, E. E., & Gross, K. L., et al. (2005). Functional- and abundance-based mechanisms explain diversity loss due to N fertilization. *Proceedings of the National Academy of Sciences of the United States of America*, 102, 4387–4392.
- Tietema, A. (1998). Microbial carbon and nitrogen dynamics in coniferous forest floor material collected along a European nitrogen deposition gradient. *Forest Ecology and Management*, 101, 29–36.
- Tietema, A., Emmett, B. A., Gundersen, P., Kjønaas, O. J., & Koopmans, C. J. (1998). The fate of ^{15}N -labelled nitrogen deposition in coniferous forest ecosystems. *Forest Ecology and Management*, 101, 19–27.
- Van't Riet, J., Stouthamer, A. H., & Planta, R. J. (1968). Regulation of nitrate assimilation and nitrate respiration in *Aerobacter aerogenes*. *Journal of Bacteriology*, 96, 1455–1464.
- Vitousek, P. M., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D., & Schlesinger, W. H., et al. (1997). Human alteration of the global nitrogen cycle: Causes and consequence. *Issues in Ecology*, 1, 1–17.
- Waldrop, P., Zak, D. R., Sinsabaugh, R. L., Gallo, M., & Lauber, C. (2004). Nitrogen deposition modifies soil carbon storage through changes in microbial enzymatic activity. *Ecological Applications*, 14, 1172–1177.
- Williard, K. W. J., DeWalle, D. R., Edwards, P. J., & Schnabel, R. R. (1997). Indicators of nitrate export from forested watersheds of the mid-Appalachians, United States of America. *Global Biogeochemical Cycles*, 11, 649–656.
- Zak, D. R., Pregitzer, K. S., Holmes, W. E., Burton, A. J., & Zogg, G. P. (2004). Anthropogenic N deposition and the fate of $(\text{NO}_3^-)\text{-}^{15}\text{N}$ in a northern hardwood ecosystem. *Biogeochemistry*, 69, 143–157.
- Zogg, G. P., Zak, D. R., Pregitzer, K. S., & Burton, A. J. (2000). Microbial immobilization and the retention of anthropogenic nitrate in a northern hardwood. *Ecology*, 81, 1858–1866.

Effects of Nitrogen Deposition on Bryophyte Species Composition of Calcareous Grasslands

B. J. Haworth · M. R. Ashmore · A. D. Headley

Received: 12 June 2005 / Accepted: 4 April 2006 / Published online: 19 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Regular additions of NH_4NO_3 (35–140 kg N ha^{-1} yr^{-1}) and $(\text{NH}_4)_2\text{SO}_4$ (140 kg N ha^{-1} yr^{-1}) to a calcareous grassland in northern England over a period of 12 years have resulted in a decline in the frequency of the indigenous bryophyte species and the establishment of non-indigenous calcifuge species, with implications for the structure and composition of this calcareous bryophyte community. The lowest NH_4NO_3 additions of 35 kg N ha^{-1} yr^{-1} produced significant declines in frequency of *Hypnum cupressiforme*, *Campylium chrysophyllum*, and *Callicteron cuspidatum*. Significant reductions in frequency at higher NH_4NO_3 application rates were recorded for *Pseudoscleropodium purum*, *Ctenidium molluscum*, and *Dicranum scoparium*. The highest NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ additions provided conditions conducive for the establishment of two typical calcifuges – *Polytrichum* spp. and *Campylopus introflexus*, respectively. Substrate-surface pH measurements showed a dose-related reduction in pH with increasing NH_4NO_3 deposition rates of 1.6 pH units between the control and highest deposition rate, and a further significant

fall in pH, of >1 pH unit, between the NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ treatments. These results suggest that indigenous bryophyte composition may be at risk from nitrogen deposition rates of 35 kg N ha^{-1} yr^{-1} or less. These effects are of particular concern for rare or endangered species of low frequency.

Keywords acidification · nitrogen deposition · bryophytes · calcareous grassland · *Campylopus introflexus* · composition · frequency · *Polytrichum*

1 Introduction

Calcareous grasslands are among the most species rich plant communities in Europe (Bobbink, Ashmore, Braun, Fluckiger, & Van den Wyngaert, 2002). They include many characteristic bryophyte species, some of which are rare and endangered. Traditional agricultural use and management has generally maintained low nutrient status and, as closed communities, calcareous grasslands, under established natural conditions, are unlikely to undergo rapid change. It is expected over the long term, however, they will be affected by the fertilizing effect of increased atmospheric nitrogen input.

Few experiments have been established with the objective of observing grassland ecosystem response to long-term nitrogen deposition rates within the range found in Europe. The main findings of these

B. J. Haworth (✉) · M. R. Ashmore
Environment Department, University of York,
York YO10 5DD, UK
e-mail: bjhaworth@tiscali.co.uk

A. D. Headley
Department of Geography and Environmental Science,
University of Bradford, Bradford, UK

experiments have been summarised in Cunha et al. (2002); in most cases in which bryophyte data have been recorded, only total cover or data for the most common species was recorded. Apart from the study of Burch (2001), little data has been obtained on changes to the individual bryophyte species in these experiments. Therefore, despite the evidence that many characteristic mosses have disappeared in recent years from calcareous grasslands in the UK (Hewins & Ling, 1998), few data are available on the effects of nitrogen deposition on the bryophyte populations of the unimproved calcareous grasslands that are typical of areas of upland Britain.

Bryophytes form an important part of the structure of upland grasslands (typically 50–60% cover), and act as a buffer for atmospheric deposition, as they absorb and may retain a significant proportion of the incoming nitrogen (Carroll et al., 2000). Changes to bryophyte composition may reduce the species diversity of the system leading to significant shifts in community structure.

The longest field manipulation experiment to assess the impacts of nitrogen deposition on upland calcareous grasslands is that at Wardlow Hay Cop in the Derbyshire Dales (Carroll et al., 2000; Carroll, Caporn, Johnson, Morecroft, & Lee, 2003; Morecroft, Sellers, & Lee, 1994), where regular spraying of nitrogen solutions has taken place over a period in excess of 10 years. The need for such long-term ecosystem manipulation experiments in order for the effects of nitrogen deposition to become apparent was emphasised at Wardlow Hay Cop, as after six years Carroll et al. (2000, 2003) measured a clear and dose-related loss of total bryophyte cover in response to increasing ammonium nitrate additions. Carroll et al. (2000) suggested that these losses in bryophyte cover are not likely to be due to changes in the competitive balance between the species or plant groups present in the plots, and that the high concentrations of nitrate ions and ammonium ions may be directly toxic to bryophyte species irrespective of the overall rate of application. More detailed bryophyte surveys were undertaken in April–May 1999 by Burch (2001) who found similar species diversity at all deposition rates apart from the highest ($140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) plots, where the diversity declined.

Another potential cause of these changes in bryophyte cover is nitrogen-related surface acidification influencing calcicole-calcifuge responses, as

decreases in soil pH were reported by Carroll et al. (2003). The rapid acidification of unlimed grasslands treated with ammonium sulphate fertilizers is a well-known phenomenon in commercial farming, although studies are primarily limited to acidic, mesotrophic and neutral grasslands (e.g. Bobbink, Hornung, & Roelofs, 1998; Koerselman & Meuleman, 1996; Roem & Berendse, 2000). The lowering of soil pH, taken together with the high levels of nitrogen, could cause changes in the species composition of calcareous grasslands either directly, or indirectly by altering nutrient availability that may disadvantage the more calcicolous species in particular (Carroll et al., 2003). There are very few studies showing acidification as an issue in terms of species diversity in calcareous grasslands.

This study aimed to extend the observations of Burch (2001), Carroll et al. (2003), Morecroft et al. (1994), and , over a much longer period, to assess the continued effects of long-term chronic additions of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ on the bryophyte species composition of the calcareous grassland at Wardlow Hay Cop. Specific aims were to address the issues of whether bryophyte response is an indirect result of nitrogen deposition causing soil surface acidification and whether the form of nitrogen applied influences species composition.

2 Materials and Methods

The field experiment was established in 1990 at Wardlow Hay Cop in the Derbyshire Peak District, UK and was operated by Sheffield and Manchester Metropolitan Universities. Detailed information on the experimental design is provided by Morecroft et al. (1994). Estimated background reactive N deposition was $19 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Morecroft et al., 1994). The plots were arranged in four randomised replicate blocks. Five $1 \times 1 \text{ m}$ plots surveyed in each block received water only (0N), 35, 70, and $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ as NH_4NO_3 , and $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ as $(\text{NH}_4)_2\text{SO}_4$. The spraying ceased in July 2002.

The survey was undertaken in May/June 2002. A $1 \times 1 \text{ m}$ quadrat subdivided into one hundred $10 \times 10 \text{ cm}$ squares was used to produce a percentage frequency for each species in each plot. Soil pH measurements were taken in the field using a portable pH meter at 15 random points in each plot. At each

point a hole was bored 2.5 cm deep and 1 cm diameter. The hole was filled with double distilled water and equilibrated for 1 min. The pH electrode was inserted into the hole and equilibrated for 1 min. The pH reading was then taken. An average reading for the plot was calculated.

The statistical calculations were undertaken in SPSS version 11.0 and were based upon the mean values for each plot. For the NH_4NO_3 treatments, a

one-way ANOVA was calculated with a multiple comparison correction (Bonferroni). Where the distribution was not normal, a Kruskal–Wallis test was performed. When comparing the $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ treatments an Independent Samples *T*-test was performed. Where distribution was not normal, an Exact Mann Whitney *U* test was performed. The mean difference between treatments was judged to be significant at $P < 0.05$ in all tests.

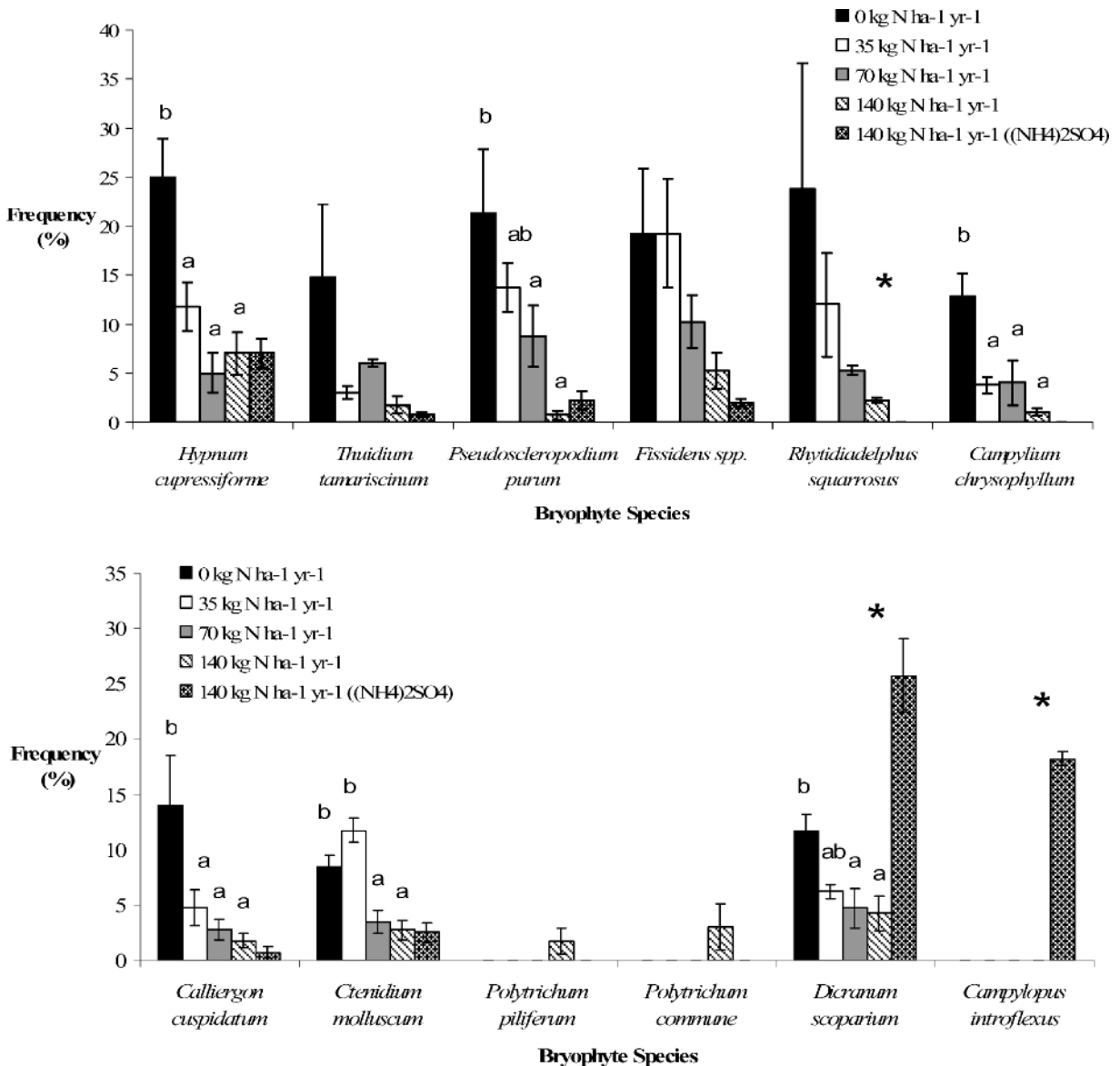


Fig. 1 The impact of increasing NH_4NO_3 deposition, and the impact of sulphate rather than nitrate at $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, on the average frequency of occurrence for key selected bryophyte species recorded during the 2002 species survey at Wardlow

Hay Cop. Error bars represent the standard error ($n=4$). Letters indicate significant difference at $P < 0.05$. Significance between nitrogen forms is denoted by *

3 Results

3.1 Species Survey

The most abundant bryophytes in the control plots were *Rhytidiadelphus squarrosus*, *Hypnum cupressiforme*, *Pseudoscleropodium purum*, and *Fissidens* spp. All bryophyte species recorded showed a response to treatment, with key species declining significantly in frequency with increasing nitrogen treatments (Fig. 1), although the threshold for significant differences from the control varied. *H. cupressiforme* ($F=12.78$; $P<0.01$), *Campylium chrysophyllum* ($F=22.17$; $P<0.001$) and *Calliergon cuspidatum* ($F=12.81$; $P<0.01$) showed significant declines at NH_4NO_3 deposition rates as low as $35 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and all higher treatments, *Ctenidium molluscum* ($F=16.68$; $P<0.01$) and *Dicranum scoparium* ($F=7.41$; $P<0.01$) declined significantly at $70 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and all higher treatments, and *P. purum* ($F=4.76$; $P<0.05$) showed a significant decline at $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$.

In an independent samples *t*-test, *R. squarrosus* showed a significant reduction ($t=9.0$; $P<0.001$) in frequency on the $(\text{NH}_4)_2\text{SO}_4$ plots compared to the NH_4NO_3 plots (Fig. 1). Two species showed a significant increase in frequency of occurrence in the $(\text{NH}_4)_2\text{SO}_4$ plots over and above their presence in

the NH_4NO_3 plots. These were *D. scoparium* ($t=-5.9$; $P<0.01$) and *Campylopus introflexus* ($t=-29.0$; $P<0.001$). *C. introflexus* was not present in any of the NH_4NO_3 treatment plots (Fig. 1).

Analysis of variance showed no significant NH_4NO_3 treatment effect ($F=0.58$; $P>0.05$) on species diversity, nor was any significant effect of replacing nitrate with sulphate at $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ($t=0.87$; $P>0.05$) recorded by means of an independent samples *t*-test. There were, however, major differences in the species appearing in the different plots. For example, *C. introflexus* and *Polytrichum* spp. appeared in the $(\text{NH}_4)_2\text{SO}_4$ and higher NH_4NO_3 plots respectively, whereas species such as *R. squarrosus* and *C. chrysophyllum* disappeared from the $(\text{NH}_4)_2\text{SO}_4$ plots (Fig. 1).

3.2 Soil pH Measurements

Analysis of variance for the soil pH values showed a highly significant treatment effect of NH_4NO_3 ($F=241.0$; $P<0.001$), with a fall in pH values with increasing treatment (Fig. 2). The fall in pH was broadly linear with increasing NH_4NO_3 deposition, with a more marked decrease in pH in the $(\text{NH}_4)_2\text{SO}_4$ plots. An independent samples *t*-test showed that the fall in pH values on the $(\text{NH}_4)_2\text{SO}_4$ plots, of

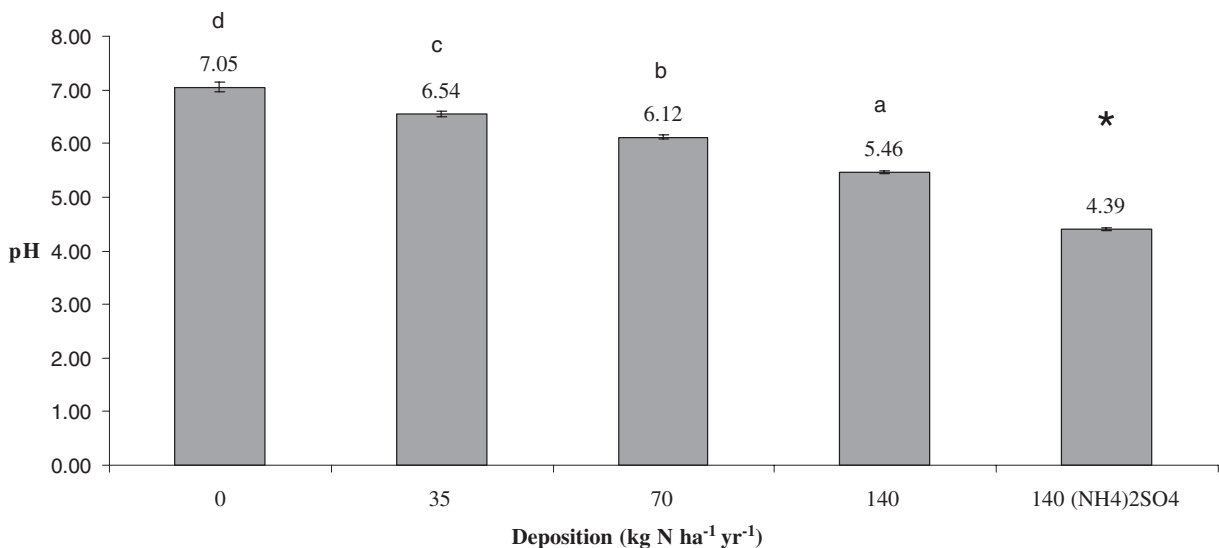


Fig. 2 The impact of increasing NH_4NO_3 and the impact of sulphate rather than nitrate at $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ on the soil pH recorded at Wardlow Hay Cop. Values are mean pH values per treatment, based on fifteen random measurements across each

treatment plot. Error bars represent the standard error ($n=4$). Letters indicate significant difference at $P<0.05$. Significance between nitrogen forms is denoted by *

approximately one pH unit, compared with the pH values for the highest NH_4NO_3 treatment ($140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), was highly significant ($t=23.4$; $P<0.001$). At each deposition rate for NH_4NO_3 , the fall in pH value was statistically significant compared to that of the next lowest deposition rate. It should be noted that considerable variation in pH was found within a single plot. The mean pH ranges for each plot (the mean of the four highest values compared to the mean of the four lowest values for each replicate plot per treatment) were typically approximately 1 pH unit, and this was independent of treatment.

4 Discussion

Long-term nitrogen deposition, in the form of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$, has clearly caused changes to the composition of the indigenous bryophyte community of a calcareous grassland at Wardlow Hay Cop, which are associated with a significant acidification of the soil surface. However, the changes in frequency of individual bryophyte species may not be causally related to acidification, and interpretation based on both the data and the known habitat preferences of the species is needed. Three distinct groups of species can be identified: – (a) those that responded negatively to NH_4NO_3 ; (b) those that responded positively to NH_4NO_3 ; and (c) those that responded positively to $(\text{NH}_4)_2\text{SO}_4$.

In group (a) several bryophyte species showed a dose-related decline in frequency in response to NH_4NO_3 . Due to their wide ecological tolerance, it is unlikely that *R. squarrosus*, *P. purum*, and *H. cupressiforme*, which showed a decline in frequency in response to NH_4NO_3 , and, in the case of *R. squarrosus*, disappeared completely with $(\text{NH}_4)_2\text{SO}_4$, were responding to the decrease in substrate pH. Nor were these responses accompanied by a detectable increase in higher plant cover. It is hypothesised, therefore, that, NH_4NO_3 at higher deposition rates and $(\text{NH}_4)_2\text{SO}_4$ were having a direct toxic effect on the metabolic processes of these species.

In contrast, *C. cuspidatum*, *T. tamariscinum*, *C. molluscum*, *Fissidens* spp., and *C. chrysophyllum* are all calcicoles. The general decline in frequency for these species with increasing NH_4NO_3 deposition and the small presence, if any, in the $(\text{NH}_4)_2\text{SO}_4$ plots suggests that the response may be due to the effect of

pH. This is consistent with respect to *C. cuspidatum* with the work of Streeter (1970), who showed that this species has a strong preference for pH values around neutrality and will not grow below pH 6, even if the calcium concentration is increased.

The effect of pH change on species composition has also been to facilitate the invasion of non-native species, such as *P. commune* and *P. piliferum*, in group (b). Both of these species are calcifuges and rare in calcareous areas. Their appearance within some high concentration NH_4NO_3 plots, although statistically insignificant, demonstrates the surface acidification process caused by high levels of NH_4NO_3 deposition and its potential impacts upon species composition, especially as the *Polytrichum* spp. appeared within the micro-pockets of lowest pH within these plots. It is unclear whether pH is the sole factor responsible for the appearance of *Polytrichum* spp., however, as these species do not appear in the $(\text{NH}_4)_2\text{SO}_4$ plots. However, *P. commune* has previously appeared more resistant to quick-dissolving solid fertilizers where other species have declined (for example, Jäppinen & Hotanen, 1990), and may be taking advantage of a breakdown in the structure of the grassland community.

In group (c), *D. scoparium* can occur on leached calcareous grassland but is a common calcifuge (Watson, 1968). The significant increase in frequency for *D. scoparium* suggests that the low surface pH caused by the addition of $(\text{NH}_4)_2\text{SO}_4$ was creating a more favourable growing environment for this species. It is possible that changes in vegetation cover due to changes in soil chemistry such as acidification or, perhaps, vegetation palatability, thus leaving disturbed or bare patches of ground, together with the acidification of the soil in the $(\text{NH}_4)_2\text{SO}_4$ plots, may have created the necessary conditions for the colonisation by *C. introflexus*, a classic calcifuge and colonist of bare acidic substrate. The fact that the results show that *C. introflexus* does not appear in any of the NH_4NO_3 plots but only in the $(\text{NH}_4)_2\text{SO}_4$ plots, where acidification has occurred to the greatest degree, suggests that the decrease in pH and changes to the vegetation structure might be the prime factors in the establishment of this species.

The clear, significant dose-related acidification on the calcareous plots with increasing NH_4NO_3 treatments, and the further effect in the $(\text{NH}_4)_2\text{SO}_4$ treatments, is consistent with the data of Carroll et al.

(2003) who suggested that the very high rates of nitrification obtained during the summer months may be a cause of the decline in the pH of the soil, and particularly in the $(\text{NH}_4)_2\text{SO}_4$ plots. However, the size of the pH difference was found to be much greater in this study than in the Carroll et al. (2003) study, who measured a difference of 0.7 pH units between the control and $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ plots and a further 0.9 pH unit drop in the $(\text{NH}_4)_2\text{SO}_4$ plots compared to the high NH_4NO_3 plots. This is probably due to the greater depth of soil sampled in the Carroll et al. (2003) study, in contrast to this study which focussed on the surface layer, of most relevance to bryophytes.

Considerable variation in acidity was found within a single plot, which may be accounted for by small scale variation influencing the ability of the substrate to buffer increases in acidity. In the plots where non-indigenous bryophyte species were being recorded, such as *Polytrichum spp.*, these species could be found at points of lowest pH. In this respect, *Polytrichum spp.* is acting as a biological indicator of low pH.

In terms of the group (a) bryophytes, as the soil acidifies, toxic levels of micronutrients may become available in solution. Those bryophytes in direct contact with the surface soil layer would be more prone to the effects of any increase of toxic elements in solution, though nutrient flow from underlying litter has been implicated as a significant factor in a study of grassland bryophytes by Rincón (1988). Ions can move to the bryophyte apices through the apoplast system under the influence of an evaporative moisture flow, meaning that bryophytes that exist on the litter surface rather than in direct soil contact may still receive solubilized mineral nutrition from the underlying substrate.

5 Conclusions

Nitrogen deposition in the forms of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ has been shown to cause a detrimental response in the indigenous bryophyte community of a calcareous grassland, with a marked calcicole-calcifuge shift in bryophyte species composition. The relative significance of different mechanisms involved in changes to the bryophyte composition are not clear at this stage, and are likely to differ between species.

The additional nitrogen inputs are clearly associated with a dose-related effect on some aspect of the growth or survival of the bryophyte population, with responses being observed at treatment concentrations as low as $35 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. A number of rare bryophyte species occur in calcareous grasslands, such as *Weissia sterilis*, and such low-frequency bryophytes with a specialised niche could be at risk of disappearing from calcareous communities. However, whereas some species of bryophyte decline or disappear with increasing concentrations of NH_4NO_3 and addition of $(\text{NH}_4)_2\text{SO}_4$, other species start to appear and, in some cases, thrive. It is suggested, therefore, that a number of factors are responsible for the varying results seen for different species. These are (a) direct nitrogen toxicity; (b) acidification (reduced pH); (c) solubilisation of micronutrients to toxic levels. The time-scale of the response may indicate a direct effect on metabolic processes rather than long-term nitrogen accumulation in the ecosystem, and this has implications for rates of both response and recovery as nitrogen deposition rates change.

Acknowledgements We are grateful to the University of Sheffield, in particular Professor J. Lee and Dr. G. Phoenix, and Manchester Metropolitan University, in particular Dr. S. Caporn and Dr J. Carroll for the use of the long-term field site at Wardlow Hay Cop. We are also grateful to the Department of the Environment, Food, and Rural Affairs for a studentship to B. J. Haworth.

References

- Bobbink, R., Ashmore, M., Braun, S., Flückiger, W., & Van den Wyngaert, I. J. J. (2002). Empirical nitrogen critical loads for natural and semi-natural ecosystems: 2002 update. In *Empirical critical loads for nitrogen-expert workshop*, (pp 43–170) Berne, 11–13 November 2002, Swiss Agency for the Environment, Forests and Landscape (SAEFL).
- Bobbink, R., Hornung, M., & Roelofs, J. G. M. (1998). The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. *Journal of Ecology*, 86, 717–738.
- Burch, J. A. (2001). *The Response of bryophytes to elevated atmospheric deposition of nitrogen*, PhD Thesis (273). Department of Animal and Plant Sciences, University of Sheffield.
- Carroll, J. A., Caporn, S. J. M., Johnson, D., Morecroft, M. D., & Lee, J. A. (2003). The interactions between plant growth, vegetation structure and soil processes in semi-natural acidic and calcareous grasslands receiving long-term inputs of simulated pollutant nitrogen deposition. *Environmental Pollution*, 121, 363–376.

- Carroll, J. A., Johnson, D., Morecroft, M., Taylor, A., Caporn, S. J. M., & Lee, J. A. (2000). The effect of long-term nitrogen additions on the bryophyte cover of upland acidic grasslands. *Journal of Bryology*, 22, 83–89.
- Cunha, A., Power, S. A., Ashmore, M. R., Green, P. R. S., Haworth, B. J., & Bobbink, R. (2002). *Whole ecosystem nitrogen manipulation – an updated review, report no. 331*. Peterborough, UK: Joint Nature Conservation Committee.
- Hewins, E. J., & Ling, K. A. (1998). *The impacts of management and atmospheric ammonia deposition on plant communities of calcareous grasslands, Book of Abstracts*. Rothamsted: CAPER.
- Jäppinen, J. P., & Hotanen, J. P. (1990). Effect of fertilization on the abundance of bryophytes in two drained peatland forests in Eastern Finland. *Annales Botanici Fennici*, 27, 93–108.
- Koerselman, W., & Meuleman, A. F. M. (1996). The vegetation N:P ratio: a new tool to detect the nature of nutrient limitation. *Journal of Applied Ecology*, 33, 1441–1450.
- Morecroft, M. D., Sellers, E. K., & Lee, J. A. (1994). An experimental investigation into the effects of atmospheric nitrogen deposition on two semi-natural grasslands. *Journal of Ecology*, 82, 475–483.
- Rincón, E. (1988). The effect of herbaceous litter on bryophyte growth. *Journal of Bryology*, 15, 209–217.
- Roem, W. J., & Berendse, F. (2000). Soil acidity and nutrient supply ratio as possible factors determining changes in plant species diversity in grassland and heathland communities. *Biological Conservation*, 92, 151–161.
- Streeter, D. T. (1970). Bryophyte ecology. *Science Progress*, 58, 419–434.
- Watson, E. V. (1968). *British mosses and liverworts*. Cambridge, UK: Cambridge University Press.

Atmospheric Deposition of Reactive Nitrogen on Turf Grassland in Central Japan: Comparison of the Contribution of Wet and Dry Deposition

Kentaro Hayashi · Michio Komada · Akira Miyata

Received: 23 June 2005 / Accepted: 29 March 2006 / Published online: 19 January 2007
© Springer Science + Business Media B.V. 2007

Abstract The atmospheric deposition of reactive nitrogen on turf grassland in Tsukuba, central Japan, was investigated from July 2003 to December 2004. The target components were ammonium, nitrate, and nitrite ions for wet deposition and gaseous ammonia, nitric and nitrous acids, and particulate ammonium, nitrate, and nitrite for dry deposition. Organic nitrogen was also evaluated by subtracting the amount of inorganic nitrogen from total nitrogen. A wet-only sampler and filter holders were used to collect precipitation and the atmospheric components, respectively. An inferential method was applied to calculate the dry deposition velocity of gases and particles, which involved the effects of surface wetness and ammonia volatilization through stomata on the dry deposition velocity. The mean fraction of the monthly wet to total deposition was different among chemical species; 37, 77, and 1% for ammoniacal, nitrate-, and nitrite-nitrogen, respectively. The

annual deposition of inorganic nitrogen in 2004 was 47 and 48 mmol m⁻² yr⁻¹ for wet and dry deposition, respectively; 51% of atmospheric deposition was contributed by dry deposition. The annual wet deposition in 2004 was 20, 27, and 0.07 mmol m⁻² yr⁻¹, and the annual dry deposition in 2004 was 35, 7.4, and 5.4 mmol m⁻² yr⁻¹ for ammoniacal, nitrate-, and nitrite-nitrogen, respectively. Ammoniacal nitrogen was the most important reactive nitrogen because of its remarkable contribution to both wet and dry deposition. The median ratio of the organic nitrogen concentration to total nitrogen was 9.8, 17, and 15% for precipitation, gases, and particles, respectively.

Keywords dry deposition · inferential method · inorganic nitrogen · organic nitrogen · reactive nitrogen · turf grassland · wet deposition

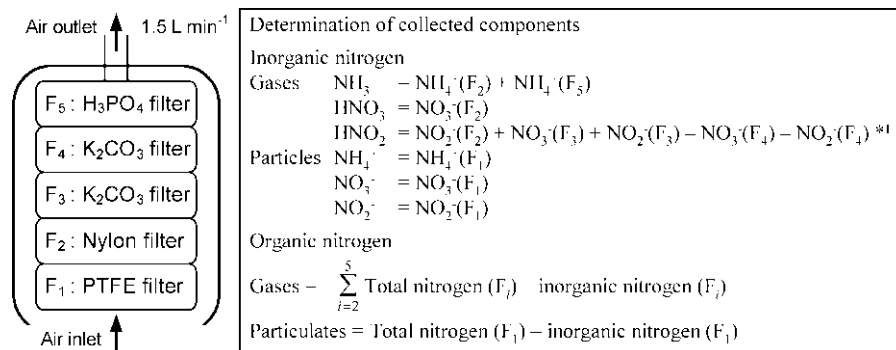
K. Hayashi (✉) · M. Komada
Carbon and Nutrient Cycles Division,
National Institute for Agro-Environmental Sciences,
3-1-3, Kan-nondai, Tsukuba,
Ibaraki 305-8604, Japan
e-mail: kentaro@affrc.go.jp

A. Miyata
Agro-Meteorology Division,
National Institute for Agro-Environmental Sciences,
3-1-3, Kan-nondai, Tsukuba,
Ibaraki 305-8604, Japan

1 Introduction

The atmospheric deposition of reactive nitrogen is an important process in the nitrogen cycle, in which excess loads have the potential to result in the nitrogen saturation of ecosystems (Aber, Nadelhoffer, Steudler, & Melillo, 1989). The quantification of deposition is, therefore, necessary to evaluate the risk of nitrogen saturation. Reactive nitrogen in the atmosphere mainly consists of ammoniacal nitrogen (NH_x), i.e., ammonia (NH₃) and ammonium ion

Fig. 1 Configuration of the holder for the set of filters used for air concentration monitoring. *¹ The K_2CO_3 filter also absorbs a fraction of NO_2 (Noguchi, personal communication). It was assumed that the F_3 stage collected both HNO_2 and NO_2 and the F_4 stage collected only NO_2



(NH_4^+) , nitrate-nitrogen ($NO_3\text{-N}$), i.e., nitric acid (HNO_3) and nitrate ion (NO_3^-), nitrite-nitrogen ($NO_2\text{-N}$), i.e., nitrous acid (HNO_2) and nitrite ion (NO_2^-) and other nitrogen oxides such as nitrogen dioxide (NO_2) and nitric oxide (NO). Furthermore, organic nitrogen also exists in the atmosphere (Keene et al., 2002).

Atmospheric deposition is divided into wet and dry deposition. The quantification of dry deposition is difficult compared to that of wet deposition. The degree of difficulty is mainly due to the fluctuation of the dry deposition velocity (V_d) along with changes in the meteorological and surface conditions; V_d is also different among chemical species and forms. Quantitative information on the dry deposition of reactive nitrogen is insufficient particularly in Japan; however, several studies on oxidized nitrogen are available (e.g., Matsuda, Fukuzaki, & Maeda, 2001; Takahashi, Sato, Wakamatsu, & Fujita, 2001). Given the circumstances, the objective of this study was to obtain fundamental information on the wet and dry deposition of reactive nitrogen in Japan.

2 Materials and Methods

2.1 Research Field

Monitoring was conducted from July 2, 2003 to December 31, 2004, at a meteorological observation field at the National Institute for Agro-Environmental Sciences (lat.36°01'N, lon.140°07'E, El. 22 m) in Tsukuba, a rural area in central Japan. The research field was covered with artificial grassland mainly composed of *Zoysia japonica* (Japanese turf). The height of vegetation was maintained at approximately 10 cm.

2.2 Wet Deposition Monitoring

A wet-only sampler with refrigerated storage (Ogasawara, US-330) was installed at a height of 5 m from the ground on the rooftop of a building located in the north corner of the research field. Precipitation samples were collected for each rain event. The precipitation concentrations of inorganic nitrogen and total nitrogen were determined by the ion chromatograph method (Yokogawa, IC7000) and the chemiluminescence method (Shimadzu, TOC-V CSH/TNM-1), respectively. The difference between total and inorganic nitrogen was qualified as organic nitrogen in precipitation.

2.3 Air Concentration Monitoring and Meteorological Observation

Weekly monitoring for air concentration was conducted at a height of 5 m from the ground, i.e., in the same plot used for wet deposition, until June 29, 2004. After that, it was conducted at a height of 2 m over the grassland using a meteorological tower in the research field. The distance between the two plots was about 50 m. Filter holders (NILU, NL-O) were used to collect reactive nitrogen in ambient air. The holder for the set of filters (Fig. 1) included five stages of filters with a diameter of 47 mm as follows: a PTFE filter (Advantec, T080A047A); a nylon filter (Pall, Nylasorb); two K_2CO_3 -impregnated cellulose filters (Advantec, 51A); and a H_3PO_4 -impregnated cellulose filter. For the PTFE filters, the collected substances were extracted by 30 min of ultrasonic cleaning with the addition of 40 mL of deionized water. For the other filters, extractions were conducted by adding 40 mL of deionized water. The same methods for

precipitation samples were applied to determine the concentrations of reactive nitrogen in the extracted solutions. The collected quantities of each component were determined by using the equations shown in Fig. 1. The weekly mean air concentrations were calculated by dividing the collected quantity by the integrated airflow.

Additional weekly monitoring for the NH_x air concentration was simultaneously conducted at the two plots to examine the differences in weekly concentration for 15 weeks from June 20 to October 3, 2005. As a result, a strong correlation in the weekly mean NH_x concentrations was found between the two plots, with correlation coefficients of 0.978 and 0.997 for NH_3 and particulate NH_4^+ , respectively. The weekly mean NH_x concentrations at a height of 5 m from the ground on the rooftop of the building closely approximated those at a height of 2 m over the grassland; the former was $3 \pm 3\%$ larger and $4 \pm 2\%$ smaller than the latter on average for NH_3 and particulate NH_4^+ , respectively ($n=15$, $p<0.05$). According to the results, the weekly mean concentrations of inorganic nitrogen on the rooftop of the building were directly applied to calculate the weekly dry deposition before June 29, 2004, without correction, assuming a similar degree of error for NH_x .

The hourly data of precipitation during the entire research period and the temperature, relative humidity, and global solar radiation until August 13, 2004, were obtained from the Weather Data Acquisition System of the National Institute for Agro-Environmental Sciences, which was at a distance of approximately 350 m from the tower on the grassland. Ten-minute data of wind direction and velocity until August 13, 2004, were obtained from the nearest weather station (lat.36°03'N, lon.140°08'E). After August 14, 2004, a meteorological observation at the research field was conducted for the wind direction and velocity (Yokogawa, A-733 and M-821), temperature and relative humidity (Vaisala, HMP45D), surface wetness (Eko, MH-045), and global solar radiation (Eko, MS-62).

2.4 Calculation of the Dry Deposition Velocity

An inferential method (e.g., Hicks, Baldocchi, Meyers, Hosker, & Matt, 1987) was applied to calculate the V_d of gasses, i.e., NH_3 , HNO_3 , and HNO_2 , and particles,

i.e., NH_4^+ , NO_3^- , and NO_2^- . For gasses, V_d at a height of z m, $V_d(z)$ (m s^{-1}), is expressed by (Sutton, Burkhardt, Guerin, Nemitz, & Fowler, 1998),

$$V_d(z) = (R_a(z) + R_b + R_c)^{-1}, \quad (1)$$

where R denotes the resistance against dry deposition (s m^{-1}). $R_a(z)$, R_b , and R_c denote the aerodynamic resistance at z m, 2 m in this study, the semi-laminar resistance, and the surface resistance, respectively. R_c is expressed by (Sutton et al., 1998),

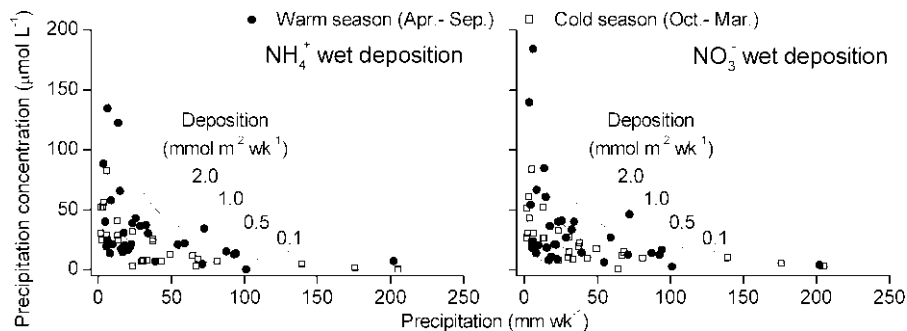
$$R_c = (R_{stom}^{-1} + R_{cut}^{-1} + R_{soil}^{-1})^{-1}, \quad (2)$$

where R_{stom} and R_{cut} denote the stomata resistance and the cuticular resistance of plant leaves, respectively, and R_{soil} is the soil surface resistance. However, V_d apparently decreases for gasses being emitted from the surface, such as NH_3 , due to the counterbalance between deposition and emission. The effect of NH_3 volatilization through plant stomata was considered by taking the concept of the compensation point (Farquhar, Firth, Wetselaar, & Weir, 1980) into the inferential method. The V_d of NH_3 is expressed by (modifying Sutton et al., 1998),

$$V_d(z) = \left(1 - C_{stom} \cdot C(z)^{-1} \cdot R_c \cdot R_{stom}^{-1}\right) \cdot (R_a(z) + R_b + R_c)^{-1}, \quad (3)$$

where C_{stom} and $C(z)$ denote the gas-phase concentration of NH_3 in stomata and the air concentration of NH_3 at a height of z m, respectively. C_{stom} is a function of the aqueous-phase NH_4^+ concentration and pH in the plant apoplast and the temperature (Schjoerring, Husted, & Mattsson, 1998). In this study, the aqueous-phase NH_4^+ concentration and pH of the plant apoplast were set as $3 \cdot 10^{-4} \text{ mol L}^{-1}$ and $1.259 \cdot 10^{-6} \text{ mol L}^{-1}$ (=pH 5.9), respectively, according to a study of *Arrhenatherum elatius*, a species of poaceous grass found in nitrogen-rich land (Hanstein, Mattsson, Jaeger, & Schjoerring, 1999). R_a is expressed by a function of the mean horizontal wind velocity and friction velocity (Hicks et al., 1987). R_a was calculated by using 10-min meteorological data. The meteorological data before August 13, 2004 were converted into those at the research field by using the converting equations derived from the simultaneous

Fig. 2 Weekly wet deposition of inorganic nitrogen



data after August 14, 2004. R_b is expressed by a function of the friction velocity, the von Karman constant, and the ratio of the Schmidt number to the Prandtl number (Hicks et al., 1987). The approximating equation of Wesely (1989) was applied to determine R_{stom} . The basic values of R_{stom} in the research field were set by referring to the values for grazing land (Wesely, 1989) as follows: 240 s m^{-1} in March, 120 s m^{-1} from April to October, and 9999 s m^{-1} from November to February. R_{cut} and R_{soil} were considered to be 0 when the surface was wet (Takahashi, Sato, Wakamatsu, Fujita, & Yoshikawa, 2002). In the case of dry conditions, R_{cut} and R_{soil} were determined by using the parameterization of Sutton, Asman, and Schjoerring (1994) and Erisman, Pul, and Wyers (1994), respectively.

The empirical equations of Wesely, Cook, Hart, and Speer (1985) were applied to infer the V_d of particles ($V_{d \text{ particle}}$), which were derived from their observations of particulate sulfate on grassland.

$$V_{d \text{ particle}}(z) = [(1/0.002 u_* + R_a(z))^{-1}] \quad (4a)$$

(Neutral or stable conditions)

$$V_{d \text{ particle}}(z) = [(1/0.01 u_* + R_a(z))^{-1}] \quad (4b)$$

(Unstable conditions)

The stability of the atmosphere was set to be unstable when the global solar radiation exceeded 100 W m^{-2} and the standard deviation of changes in wind direction exceeded 0.218 rad (12.5°); otherwise, the stability was set to be neutral or stable. The V_d for particles was considered to be equal regardless of the chemical species.

2.5 Calculation of the Deposition

The deposition for inorganic nitrogen was calculated. The wet deposition in each rain event was obtained by multiplying the precipitation concentration by the meteorologically observed precipitation. The weekly values for wet deposition, volume-weighted mean concentration, and precipitation were then calculated. In the case of a rainless week, both wet deposition and precipitation were considered to be zero. On the other hand, the weekly dry deposition was obtained by multiplying the weekly mean air concentration by the weekly mean V_d derived from the hourly values of V_d during the week. The cumulated values of monthly wet and dry deposition were also calculated.

3 Results and Discussion

3.1 Wet Deposition of Inorganic Nitrogen

The monitoring results of the weekly wet deposition of NH_4^+ and NO_3^- are shown in Fig. 2; NO_2^- was excluded due to the very small or negligible values. Table 1 summarizes the arithmetic means during the research period. Precipitation occurred in most weeks in the research field; however, the frequency and the amount were generally low and small, respectively, in winter from December to February. However, in the case of dividing 1 year into two seasons, i.e., the warm season from April to September (WS) and the cold season from October to March (CS), the mean weekly precipitation in WS, 31 mm wk^{-1} , was similar to that in CS, 30 mm wk^{-1} (Table 1), mainly due to the heavy rain as a result of typhoons, particularly in

Table 1 Arithmetic means of the atmospheric deposition of inorganic nitrogen derived from the weekly means during the research period from July, 2003 to December, 2004 ($n=79$)

Season ^d	NH ₄ ⁺ ^a		NO ₃ -N ^b		NO ₂ -N ^c		Total	
	WS	CS	WS	CS	WS	CS	WS	CS
Deposition [mmol m ⁻² wk ⁻¹]								
Wet	0.62	0.27	0.63	0.36	0.001	0.002	1.3	0.63
Dry (gas)	0.81	0.53	0.20	0.035	0.11	0.10	1.1	0.67
Dry (particle)	0.040	0.038	0.024	0.024	0.000	0.000	0.062	0.063
Total	1.4	0.84	0.84	0.42	0.11	0.11	2.4	1.4
Precipitation concentration [mmol m ⁻³] ^e	20	8.9	20	12	0.02	0.06		
Precipitation [mm wk ⁻¹]	31	30	31	30	31	30		
Air concentration [nmol m ⁻³]								
Gas	194	140	42	8.3	33	45		
Particle	89	110	53	68	0.15	0.21		
Gas/total ratio [%]	69	57	45	11	100	100		
Dry deposition velocity [cm s ⁻¹]								
Gas	0.71	0.63	0.87	0.73	0.57	0.40		
Particle ^f	0.076	0.058	0.076	0.058	0.076	0.058		

^a NH₄⁺ denotes NH₄⁺, NH₃, and particulate NH₄⁺ for wet, dry (gas), and dry (particle) deposition, respectively.

^b NO₃-N denotes NO₃⁻, HNO₃, and particulate NO₃⁻ for wet, dry (gas), and dry (particle) deposition, respectively.

^c NO₂-N denotes NO₂⁻, HNO₂, and particulate NO₂⁻ for wet, dry (gas), and dry (particle) deposition, respectively.

^d Season: WS and CS denote warm season (from April to September, $n=39$) and cold season (from October to March, $n=40$), respectively, from July 2, 2003 to December 31, 2004.

^e The precipitation concentration indicates the volume-weighted mean. On the other hand, rainless weeks were included when calculating the wet deposition and precipitation as a zero value.

^f The same deposition velocity was assumed for particles regardless of the chemical species.

October, 2004. In WS, the mean wet deposition of NO₃⁻, 0.62 mmol m⁻² wk⁻¹, was similar to that of NH₄⁺, 0.61 mmol m⁻² wk⁻¹. On the other hand, in CS, the mean wet deposition of NO₃⁻, 0.36 mmol m⁻² wk⁻¹, was larger than that of NH₄⁺, 0.27 mmol m⁻² wk⁻¹ (Table 1), which was ascribed to the relatively large decrease in the precipitation concentration of NH₄⁺ in CS compared to that of NO₃⁻ (Fig. 2 and Table 1).

The weekly wet deposition shown here is the cumulative value for every rain event during the week and is different from the values obtained by weekly sampling. According to Gilliland, Butler, and Likens (2002), the volume-weighted mean concentrations of the daily sampling were 9.9% higher and 2.6% lower than the concentrations of the weekly sampling for NH₄⁺ and NO₃⁻, respectively. In this study, the wet samples were collected immediately after each rain event; thus, the results of this study are considered to approximate those obtained by daily sampling. On the other hand, the wet-only sampler was designed to collect precipitation in case of detecting droplets of

rainwater, and it was impossible to collect fog water on the ground. Therefore, the wet deposition shown here was likely to underestimate the actual wet deposition by the fog deposition. However, quantitative information on the contribution of the occult (fog/cloud) deposition (Vermeulen et al., 1997) to the total wet deposition is insufficient, particularly in Japan. In addition, atmospheric deposition accompanying dew and frost induced by condensation and sublimation, respectively, of the water vapor in the air should be categorized as a process of dry deposition.

3.2 Dry Deposition of Inorganic Nitrogen

The estimated weekly dry deposition of NH₃, HNO₃, and HNO₂ is shown in Fig. 3, and their arithmetic means during the research period are shown in Table 1. NH₃ was the dominant gaseous nitrogen that accounted for 72 and 79% of the total gaseous dry deposition in WS and CS, respectively (Table 1). In WS, both the air concentrations and V_d of NH₃ and HNO₃ were larger than those in CS, which contributed

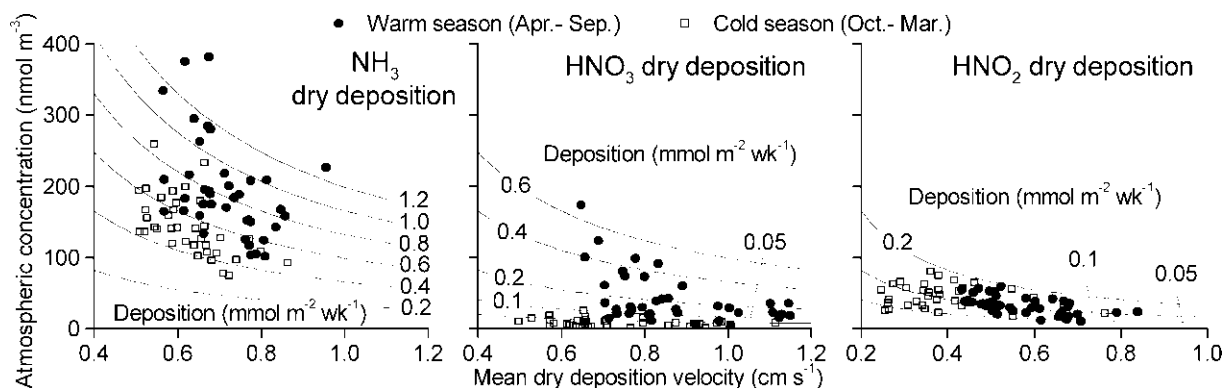


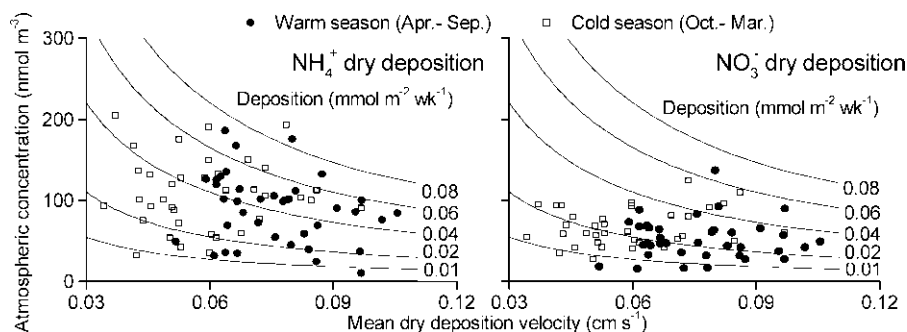
Fig. 3 Weekly dry deposition of gaseous inorganic nitrogen

to the larger gaseous dry deposition in WS (Fig. 3). Although the mean V_d of HNO₃ was larger than that of NH₃, the lower air concentration of HNO₃, which was 1/5 and 1/17 of NH₃ on average in WS and CS, respectively, resulted in less dry deposition of HNO₃ (Table 1). On the other hand, the estimated weekly dry deposition of particulate NH₄⁺ and NO₃⁻ is shown in Fig. 4 and summarized in Table 1; particulate NO₂⁻ was excluded due to the very small or negligible values. The dry deposition of NH₄⁺ was 1.6 times larger than that of NO₃⁻ on average for both WS and CS. However, the dry deposition of NH₄⁺ only accounted for 5 and 7% of the total dry deposition of NH_x in WS and CS, respectively, while the dry deposition of NO₃⁻ accounted for 10 and 40% of the total dry deposition of NO₃-N in WS and CS, respectively (Table 1). In total, the gaseous dry deposition was the dominant process that contributed up to 95 and 94% of the total dry deposition on average in WS and CS, respectively (Table 1).

The air concentrations of NH₃ in WS were higher than those in CS (Fig. 3), on average, 190 and 140 nmol m⁻³ in WS and CS, respectively (Table 1). The main reason can be ascribed to the higher

temperatures in WS. A higher temperature enhances the dissociation of particulate NH₄⁺ in the air, such as ammonium chloride (NH₄Cl) and ammonium nitrate (NH₄NO₃), to liberate NH₃; this tendency is more remarkable for NH₄Cl than for NH₄NO₃ (Kaneyasu, Yoshikado, Mizuno, Sakamoto, & Soufuku, 1999). Furthermore, a higher temperature enhances the dissociation of aqueous-phase NH₄⁺ to liberate NH₃ and influences the Henry's law constant for NH₃ (Jayaweera & Mikkelsen, 1990), both of which facilitate NH₃ volatilization from emitters, such as livestock excreta and croplands with nitrogen fertilization. However, the research field was unlikely to be an NH₃ emitter because of the lack of fertilization. The air concentrations of HNO₃ were clearly high in WS (Fig. 3), on average 41 and 8.3 nmol m⁻³ in WS and CS, respectively (Table 1). Inversely, the air concentrations of HNO₂ were slightly low in WS (Fig. 3), on average, 32 and 45 nmol m⁻³ in WS and CS, respectively (Table 1). The important formation processes of HNO₃ are reaction of NO₂ with OH radical, generation from NO₃ radical, and generation from N₂O₅ (Russell, McRae, & Cass, 1985). Higher formation rates of these radicals were expected in WS

Fig. 4 Weekly dry deposition of particulate inorganic nitrogen



accompanying higher temperature and more intensive solar radiation than in CS, which contributed to the higher air concentrations of HNO_3 in WS. On the other hand, for HNO_2 , both formation and loss processes exist in the air, including the heterogeneous reactions between land surface and the atmosphere (Stutz, Alicke, & Neftel, 2002). The main loss process of HNO_2 during the day is photolysis, which is enhanced by stronger ultraviolet radiation (Stutz et al., 2002), such as in WS. It is considered that the HNO_2 photolysis partly contributed to the slightly lower air concentrations of HNO_2 in WS compared with those in CS. However, the methodology for determining the air concentration of HNO_3 and HNO_2 using the filter holder (Fig. 1) needs further investigation to improve its accuracy.

It is generally considered that the V_d of gases decreases in CS due to the inactivity of plants that absorb gaseous nitrogen through stomata. However, no clear differences in V_d between WS and CS were shown for NH_3 (Fig. 3 and Table 1). This was ascribed to the counterbalance by the NH_3 emission through plant stomata to some extent, which was active in WS and depressed the net dry deposition of NH_3 . HNO_3 also showed a weak difference in V_d between WS and CS (Fig. 3 and Table 1). This was attributed to the negligible values of R_{cut} and R_{soil} to HNO_3 (Erisman et al., 1994) that resulted in an almost zero R_c to HNO_3 regardless of the fluctuations in R_{stom} .

Taking into consideration that V_d varies accompanying a change in surface conditions, the arithmetic means of the hourly V_d divided into several categories, i.e., surface wetness, day and night, and season, are also shown in Table 2. The mean V_d of NH_3 , which ranged from 0.55 to 0.93 cm s^{-1} , was smaller than that reported in early studies, e.g., 1.6 cm s^{-1} over a neutral cut meadow (Sutton, Fowler, & Moncrieff, 1993), 1.9 cm s^{-1} over heathland on average (Duyzer, 1994), and 1.3 cm s^{-1} over an alpine tundra (Ratray & Sievering, 2001). The small R_c of NH_3 up to 50 s m^{-1} means that the contribution of R_a and R_b , particularly R_a , to the V_d of NH_3 is large. R_a at the research field was likely to be large due to the small roughness length, 0.01 m, which probably resulted in the smaller V_d of NH_3 compared to the values in early studies. The R_c of NH_3 under dry conditions was small up to 50 s m^{-1} ; therefore, the increasing effect on V_d by assuming R_c of NH_3 as

zero under wet conditions was relatively small and likely canceled by the larger R_a under wet than dry conditions (Table 2). Furthermore, the decreasing effect on V_d by NH_3 emission through stomata was strong particularly in the daytime under dry conditions in WS. As a result of these effects, the V_d of NH_3 under wet conditions was larger than that under dry conditions in many cases, except for the daytime in CS, which was similar. The mean V_d of HNO_3 , which ranged from 0.55 to 1.2 cm s^{-1} , was smaller than that reported in early studies, e.g., 1.3 cm s^{-1} over an alpine tundra (Ratray & Sievering, 2001), 7.6 cm s^{-1} over a spruce-fir forest (Sievering, Kelly, McConville, Seibold, & Turnipseed, 2001), and 7.5 cm s^{-1} over a conifer forest (Pryor & Klemm, 2004). The V_d of HNO_3 is determined by R_a and R_b , particularly R_a , since the R_c of HNO_3 is assumed to be constantly zero. Therefore, similar to the case of NH_3 , the large R_a due to the small roughness length of the research field resulted in the relatively small V_d of HNO_3 . The rather small V_d of HNO_3 under wet conditions compared to that under dry conditions was ascribed to the relatively large R_a under wet conditions (Table 2). Inversely, the V_d of HNO_2 by assuming R_c as zero under wet conditions resulted in the larger V_d of HNO_2 under wet than dry conditions (Table 2). The much smaller V_d of particles in nighttime was resulted from the assumption that conditions were stable during the nighttime (Eq. 4a). The relatively small V_d of particles under wet than dry conditions was also ascribed to the difference in R_a between wet and dry conditions.

The uncertainty in the estimated dry deposition is a subject to be discussed. The weekly mean concentrations at a height of 5 m from the ground on the roof top of the building were likely to differ from those at a height of 2 m over the grassland by several percentage points, as mentioned in Section 2.3. Although the difference in the air concentrations was probably large for a shorter averaging time, such as an hour, the averaging time in this study, i.e., a week, was sufficiently long to smooth the fluctuation in the air concentration induced by turbulence. Thus, it was considered that the difference in the air concentrations between the two plots was acceptable for the estimation of the weekly dry deposition. Regarding the averaging time for the calculation of the dry deposition, depending on the sign of correlation, the estimated flux under- or overestimates the actual flux

Table 2 Arithmetic means of the dry deposition velocity of inorganic nitrogen for each condition derived from the hourly values during the research period from July, 2003 to December, 2004 ($n=13152$)

Season ^a	Day/Night ^b	Mean dry deposition velocity [cm s^{-1}]								Mean R_a [s m^{-1}]		n	
		NH ₃		HNO ₃		HNO ₂		Particle		Dry	Wet	Dry	Wet
		Dry ^c	Wet ^c	Dry	Wet	Dry	Wet	Dry	Wet				
WS	Day	0.74	0.93	1.2	0.81	0.51	0.84	0.15	0.10	70	104	2341	274
	Night	0.64	0.73	0.81	0.63	0.53	0.66	0.032	0.025	106	135	1742	2160
CS	Day	0.72	0.70	1.0	0.61	0.28	0.63	0.14	0.074	82	135	1827	144
	Night	0.55	0.63	0.66	0.55	0.34	0.57	0.026	0.022	132	173	2622	2042

^aSeason: WS and CS denote warm season (from April to September) and cold season (from October to March), respectively, from July 2, 2003 to December 31, 2004.

^bDay/Night: Day, global solar radiation $\geq 100 \text{ W m}^{-2}$; Night, the opposite case.

^cSurface wetness: dry conditions; wet conditions induced by precipitation, fog, or dew.

when the covariance between the air concentration and V_d is large (Clarke, Edgerton, & Martin, 1997). The dry deposition of HNO₃ in winter derived from the weekly means was similar to that derived from the hourly means, while the dry deposition of HNO₃ in summer derived from the weekly means underestimated the flux by up to 40% due to the positive correlation between the air concentration and V_d (Clarke et al., 1997). Although it was difficult to evaluate the degree of uncertainty based on the limited information, it was possible that the estimated dry deposition in this study also underestimated the actual deposition particularly in WS.

3.3 Comparison of the Wet and Dry Deposition of Inorganic Nitrogen

The monthly wet and dry deposition of inorganic nitrogen is shown in Fig. 5. The remarkably small wet deposition from December to February (Fig. 5) reflected less precipitation in winter in this region. The monthly dry deposition was also relatively large

in WS and small in CS, although the degree of changes was smaller than that of wet deposition. The monthly wet deposition was 1.9, 2.2, 0.005, and 4.1 $\text{mmol m}^{-2} \text{ month}^{-1}$ on average, and the monthly dry deposition was 3.0, 0.62, 0.46, and 4.1 $\text{mmol m}^{-2} \text{ month}^{-1}$ on average for NH_x, NO₃-N, NO₂-N, and inorganic nitrogen, respectively. The mean fraction of the monthly wet to total deposition was 37, 77, 1, and 47% for NH_x, NO₃-N, NO₂-N, and inorganic nitrogen, respectively. Hence, the contribution of wet to total deposition was comparable, dominant, and negligible for NH_x, NO₃-N, and NO₂-N, respectively.

The annual deposition in 2004 is shown in Table 3. The annual wet deposition in 2004 was 20, 27, 0.07, and 47 $\text{mmol m}^{-2} \text{ yr}^{-1}$, and the annual dry deposition in 2004 was 35, 7.4, 5.4, and 48 $\text{mmol m}^{-2} \text{ yr}^{-1}$ for NH_x, NO₃-N, NO₂-N, and inorganic nitrogen, respectively. The annual total deposition of inorganic nitrogen in 2004 was 95 $\text{mmol m}^{-2} \text{ yr}^{-1}$. The following were the top three components in the composition ratio: 37%, dry deposition of NH_x; 28%, wet deposition of NO₃⁻; and 21%, wet deposition of NH₄⁺ (Table 3). Furthermore, the contribution

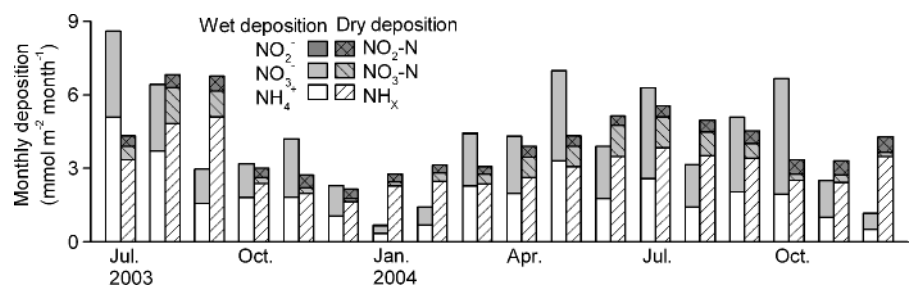
Fig. 5 Monthly wet and dry deposition of inorganic nitrogen

Table 3 Annual deposition in 2004

	Annual deposition in 2004 [$\text{mmol m}^{-2} \text{yr}^{-1}$]								Reference ^a	
	NH_x^b		$\text{NO}_3\text{-N}^c$		$\text{NO}_2\text{-N}^d$		Total		NO_2	NO
Wet	20	(21) ^e	27	(28)	0.07	(0.07)	47	(49)	–	–
Dry	35	(37)	7.4	(7.8)	5.4	(5.7)	48	(51)	24 (25)	14 (15)
Gas	33	(35)	6.0	(6.3)	5.4	(5.7)	45	(47)	24 (25)	14 (15)
Particle	2.2	(2.3)	1.4	(1.5)	0.00	(0.00)	3.6	(3.8)	–	–
Total	55	(58)	34	(36)	5.4	(5.7)	95	(100)	–	–

^aReference: The annual dry deposition of NO_2 and NO was estimated using the air concentrations observed at the nearest station for air quality monitoring, about 11 km from the research field.

^b NH_x denotes NH_4^+ , NH_3 , and particulate NH_4^+ for wet, dry (gas), and dry (particle) deposition, respectively.

^c $\text{NO}_3\text{-N}$ denotes NO_3^- , HNO_3 , and particulate NO_3^- for wet, dry (gas), and dry (particle) deposition, respectively.

^d $\text{NO}_2\text{-N}$ denotes NO_2^- , HNO_2 , and particulate NO_2^- for wet, dry (gas), and dry (particle) deposition, respectively.

^eThe values in parentheses indicate the percentage of its deposition to total deposition.

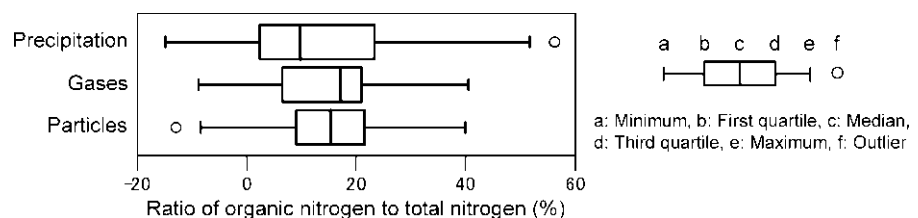
of NO_2 and NO to dry deposition was also estimated for reference. The weekly mean air concentrations of NO_2 and NO were calculated using the hourly atmospheric concentrations of NO_2 and NO during the research period. They were obtained from the nearest monitoring station for ambient air quality, which was about 11 km from the research field. The weekly means of V_d for NO_2 and NO were also calculated using the estimated hourly V_d of NO_2 and NO at a height of 2 m above the research field using Eq. 2. However, for NO , its large mesophyll resistance, R_m , was added to R_{stom} in Eq. 2 by referring to Wesely (1989). Finally, the weekly dry deposition of NO_2 and NO were calculated. The annual values of NO_2 and NO in 2004 were as follows: annual mean air concentration, 590 and 470 nmol m^{-3} ; annual mean V_d , 0.13 and 0.094 cm s^{-1} ; and annual dry deposition, 24 and 14 $\text{mmol m}^{-2} \text{yr}^{-1}$, respectively. It is concluded that the dry deposition of NO_2 and NO , particularly NO_2 , should also be evaluated since the dry deposition of NO_2 was on par with the wet deposition of NH_4^+ and NO_3^- .

3.4 Composition Ratio of Organic Nitrogen

The annual wet deposition of total nitrogen in 2004, 56 $\text{mmol m}^{-2} \text{yr}^{-1}$, exceeded that of inorganic nitrogen by 9.5 $\text{mmol m}^{-2} \text{yr}^{-1}$. This result implied that organic nitrogen accounted for 17% of the wet deposition of reactive nitrogen. On the other hand, the quantification of dry deposition of organic nitrogen was excluded from this study due to the difficulty in inferring both the V_d and air concentration of various organic nitrogen species.

The ratios of the weekly organic to total nitrogen concentrations for precipitation, gases, and particles are shown in Fig. 6. The median ratio was 9.8, 17, and 15% for precipitation, gases, and particles, respectively. Although it would be technically unfeasible to assume that the difference between inorganic and total nitrogen is attributable to organic nitrogen, the chemiluminescence method applied to determine the total nitrogen is a relatively precise method (Cornell, Jickells, Cape, Rowland, & Duce, 2003). The derived medians, therefore, perhaps approximate

Fig. 6 Percentile ranges of the composition ratios of organic nitrogen



the fact. However, it is possible that the filter holder (Fig. 1) did not collect all the gaseous organic nitrogen in the air.

4 Conclusion

From the viewpoint of the deposition load, NH_4^+ and NO_3^- were important as wet deposition and NH_3 was important as dry deposition; they occupied 86% of the total deposition of inorganic nitrogen in 2004 (Section 3.3); however, the contributions of NO_2 and NO were excluded. NH_x is the most important reactive nitrogen because of its remarkable contribution to both wet and dry deposition. The fact that organic nitrogen accounted for 17% of the annual wet deposition (Section 3.4) suggests that organic nitrogen was also an important component in precipitation. However, in future research, an effort should be made to estimate the dry deposition of organic nitrogen.

The median values of the annual wet deposition of NH_4^+ and NO_3^- in Japan during 1988–2002 were 21.5 and 26.1 $\text{mmol m}^{-2} \text{yr}^{-1}$, respectively (Hayashi et al., 2006), which were quite similar to the annual wet deposition at the research field in 2004, 20 and 27 $\text{mmol m}^{-2} \text{yr}^{-1}$, respectively. On the other hand, quantitative information of the dry deposition of reactive nitrogen is quite insufficient in Japan. In addition, the aerodynamic roughness of the research field, i.e., grassland, is smaller than that of taller vegetation, such as forests; the V_d in forests is larger than that in grassland. Therefore, despite the lack of relevant information in Japan, the quantification of NH_3 dry deposition is an important priority because of its large contribution to atmospheric deposition.

Acknowledgements We would like to express our appreciation for Dr. Izumi Noguchi, Hokkaido Institute of Environmental Sciences, Japan, and Dr. Akira Takahashi, Central Research Institute of Electric Power Industry, Japan, for their valuable comments and advice. We also thank Drs. Takayuki Saito, Yasushi Ishigooka, and Hiroaki Ikeda, National Institute for Agro-Environmental Sciences, Japan, for their cooperation with this research. The air concentration data of NO_2 and NO were provided by the National Institute for Environmental Studies and Ibaraki Prefecture.

References

- Aber, J. D., Nadelhoffer, K. J., Steudler, P., & Melillo, J. M. (1989). Nitrogen saturation in northern forest ecosystems. *BioScience*, 39, 378–386.
- Clarke, J. F., Edgerton, E. S., & Martin, B. E. (1997). Dry deposition calculations for the Clean Air Status and Trends Network. *Atmospheric Environment*, 31, 3667–3678.
- Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P., & Duce, R. A. (2003). Organic nitrogen deposition on land and coastal environments: A review of methods and data. *Atmospheric Environment*, 37, 2173–2191.
- Duyzer, J. (1994). Dry deposition of ammonia and ammonium aerosols over heathland. *Journal of Geophysical Research*, 99D9, 18757–18763.
- Erisman, J. W., Pul, A. V., & Wyers, P. (1994). Parameterization of surface resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone. *Atmospheric Environment*, 28, 2595–2607.
- Farquhar, G. D., Firth, P. M., Wetselaar, R., & Weir, B. (1980). On the gaseous exchange of ammonia between leaves and the environment: Determination of the ammonia compensation point. *Plant Physiology*, 66, 710–714.
- Gilliland, A. B., Butler, T. J., & Likens, G. E. (2002). Monthly and annual bias in weekly (NADP/NTN) versus dairy (AIRMoN) precipitation chemistry data in the Eastern USA. *Atmospheric Environment*, 36, 5197–5206.
- Hanstein, S., Mattsson, M., Jaeger, H.-J., & Schjoerring, J. K. (1999). Uptake and utilization of atmospheric ammonia in three native Poaceae species: Leaf conductances, composition of apoplastic solution and interactions with root nitrogen supply. *New Phytologist*, 141, 71–83.
- Hayashi, K., Noguchi, I., Ohizumi, T., Aikawa, M., Kitamura, M., Takahashi, A., et al. (2006). Wet deposition of inorganic nitrogen in Japan: Findings from the Japanese Acid Deposition Survey. In Z. Zhu, K. Minami, & G. Xing (Eds.), *3rd International Nitrogen Conference Contributed Papers* (pp. 598–608). NJ, USA: Science Press USA.
- Hicks, B. B., Baldocchi, D. D., Meyers, T. P., Hosker, R. P. Jr., & Matt, D. R. (1987). A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. *Water, Air, and Soil Pollution*, 36, 311–330.
- Jayaweera, G. R., & Mikkelsen, D. S. (1990). Ammonia volatilization from flooded soil systems: A computer model. I. Theoretical Aspects. *Soil Science Society of America Journal*, 54, 1447–1455.
- Kaneyasu, N., Yoshikado, H., Mizuno, T., Sakamoto, K., & Soufuku, M. (1999). Chemical forms and sources of extremely high nitrate and chloride in winter aerosol pollution in the Kanto Plain of Japan. *Atmospheric Environment*, 33, 1745–1756.
- Keene, W. C., Montag, J. A., Maben, J. R., Southwell, M., Leonard, J., Church, T. M., et al. (2002). Organic nitrogen in precipitation over Eastern North America. *Atmospheric Environment*, 36, 4529–4540.

- Matsuda, K., Fukuzaki, N., & Maeda, M. (2001). A case study on estimation of dry deposition of sulfur and nitrogen compounds by inferential method. *Water, Air, and Soil Pollution*, 130, 553–558.
- Pryor, S. C., & Klemm, O. (2004). Experimentally derived estimates of nitric acid dry deposition velocity and viscous sub-layer resistance at a conifer forest. *Atmospheric Environment*, 38, 2769–2777.
- Rattray, G., & Sievering, H. (2001). Dry deposition of ammonia, nitric acid, ammonium, and nitrate to alpine tundra at Niwot Ridge, Colorado. *Atmospheric Environment*, 35, 1105–1109.
- Russell, A. G., McRae, G. J., & Cass, G. R. (1985). The dynamics of nitric acid production and the fate of nitrogen oxides. *Atmospheric Environment*, 19, 893–903.
- Schjoerring, J. K., Husted, S., & Mattsson, M. (1998). Physiological parameters controlling plant-atmosphere ammonia exchange. *Atmospheric Environment*, 32, 491–498.
- Sievering, H., Kelly, T., McConville, G., Seibold, C., & Turnipseed, A. (2001). Nitric acid dry deposition to conifer forests: Niwot Ridge spruce-fir-pine study. *Atmospheric Environment*, 35, 3851–3859.
- Stutz, J., Alicke, B., & Neftel, A. (2002). Nitrous acid formation in the urban atmosphere: Gradient measurements of NO₂ and HONO over grass in Milan, Italy. *Journal of Geophysical Research*, 107D22, 8192.
- Sutton, M. A., Asman, W. A. H., & Schjoerring, J. K. (1994). Dry deposition of reduced nitrogen. *Tellus*, 46B, 255–273.
- Sutton, M. A., Burkhardt, J. K., Guerin, D., Nemitz, E., & Fowler, D. (1998). Development of resistance models to describe measurements of bi-directional ammonia surface-atmosphere exchange. *Atmospheric Environment*, 32, 473–480.
- Sutton, M. A., Fowler, D., & Moncrieff, J. B. (1993). The exchange of atmospheric ammonia with vegetated surfaces (I). Unfertilized vegetation. *Quarterly Journal of Royal Meteorological Society*, 119, 1023–1045.
- Takahashi, A., Sato, K., Wakamatsu, T., & Fujita, S. (2001). Atmospheric deposition of acidifying components to a Japanese cedar forest. *Water, Air, and Soil Pollution*, 130, 559–564.
- Takahashi, A., Sato, K., Wakamatsu, T., Fujita, S., & Yoshikawa, K. (2002). Estimation of dry deposition of sulfur to a forest using an inferential method: Influence of canopy wetness on SO₂ dry deposition. *Journal of Japan Society of Atmospheric Environment*, 37, 192–205. [in Japanese with English abstract]
- Vermeulen, A. T., Wyers, G. P., Römer, F. G., Van Leeuwen, N. F. M., Draaijers, G. P. J., & Erisman, J. W. (1997). Fog deposition on a coniferous forest in the Netherlands. *Atmospheric Environment*, 31, 375–386.
- Wesely, M. L. (1989). Parameterization of surface resistance to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment*, 23, 1293–1304.
- Wesely, M. L., Cook, D. R., Hart, R. L., & Speer, R. E. (1985). Measurements and parameterization of particulate sulfur dry deposition over grass. *Journal of Geophysical Research*, 90D1, 2131–2143.

Effects of Nitrogen Supply on the Sensitivity to O₃ of Growth and Photosynthesis of Japanese Beech (*Fagus crenata*) Seedlings

Masahiro Yamaguchi · Makoto Watanabe ·
Naoki Matsuo · Junichi Naba · Ryo Funada ·
Motohiro Fukami · Hideyuki Matsumura ·
Yoshihisa Kohno · Takeshi Izuta

Received: 12 June 2005 / Revised: 28 February 2006 / Accepted: 26 October 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract To obtain basic information for evaluating critical levels of O₃ under different nitrogen loads for protecting Japanese beech forests, two-year-old seedlings of *Fagus crenata* Blume were grown in potted and soil supplied with N as NH₄NO₃ solution at 0, 20 or 50 kg ha⁻¹ year⁻¹ and exposed to charcoal-filtered air or O₃ at 1.0, 1.5 and 2.0 times the ambient concentration from 16 April to 22 September 2004. The O₃ induced significant reductions in the whole-plant dry mass, net photosynthetic rate at 380 μmol

mol⁻¹ CO₂ (*A*₃₈₀), carboxylation efficiency (*CE*) and concentrations of ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) and total soluble protein (TSP) in the leaves. The concentrations of Rubisco and TSP were negatively correlated with the concentration of leaf acidic amino acid, suggesting that O₃ enhanced the degradation of protein such as Rubisco. The N supply to the soil did not significantly change the whole-plant dry mass and *A*₃₈₀, whereas it significantly increased the *CE* and concentrations of Rubisco and total amino acid. No significant interactive effects of O₃ and N supply to the soil were detected on the growth, photosynthetic parameters and concentrations of protein and amino acid in the leaves. In conclusion, N supply to the soil at ≤50 kg ha⁻¹ year⁻¹ does not significantly change the sensitivity to O₃ of growth and net photosynthesis of *Fagus crenata* seedlings.

M. Yamaguchi · M. Watanabe
United Graduate School of Agricultural Science,
Tokyo University of Agriculture and Technology,
Fuchu, Tokyo 183-8509, Japan

N. Matsuo · J. Naba
Graduate School of Agriculture, Tokyo University
of Agriculture and Technology,
Fuchu, Tokyo 183-8509, Japan

R. Funada · T. Izuta (✉)
Institute of Symbiotic Science and Technology,
Tokyo University of Agriculture and Technology,
Fuchu, Tokyo 183-8509, Japan
e-mail: izuta@cc.tuat.ac.jp

M. Fukami
Faculty of Agriculture, Utsunomiya University,
Utsunomiya, Tochigi 321-8505, Japan

H. Matsumura · Y. Kohno
Central Research Institute of Electric Power Industry,
Abiko, Chiba 270-1194, Japan

Keywords amino acid · *Fagus crenata* · growth · nitrogen · ozone · photosynthesis · Rubisco

1 Introduction

Over the midlatitudes of the Northern Hemisphere, the background ozone (O₃) level has continued to rise over the past three decades (Vingarzan, 2004). In the near future, furthermore, ground-level O₃ concentration is expected to increase in many parts of the world

as a result of the continuing rise in the emissions of precursor gases such as nitrogen oxide (Derwent, Collins, Johnson, & Stevenson, 2002). Since the ambient levels of O_3 adversely affect growth and physiological functions such as photosynthesis of forest tree species, this gas is considered to be one of the important factors relating to forest decline and tree dieback in the USA and Europe (Bytnerowicz et al., 2004; Chappelka & Samuelson, 1998). In Japan, relatively high concentrations of O_3 above 100 nl l^{-1} (ppb) have been frequently observed from spring to autumn in several mountainous areas (Maruta et al., 1999). Therefore, we must clarify the critical levels of O_3 for protecting Japanese forest ecosystems.

Excessive deposition of N such as nitrate and ammonium from the atmosphere to forest ecosystems causes soil acidification, modifies tree nutrient status and increases the sensitivity of trees to other environmental stresses such as gaseous air pollutants (Nihlgård, 1985). In Europe, the thresholds of N load for the appearance of N-saturation and forest damage are considered to be approximately 10 and $25 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively (Wright et al., 1995). In East Asia, the average nitrogen deposition of both oxidized and reduced nitrogen species is estimated to be $22 \text{ kg ha}^{-1} \text{ year}^{-1}$ and the maximum deposition would be greater than $50 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Ministry of the Environment, 2004). Therefore, there is the possibility that Japanese forest tree species are adversely affected by excessive N deposition.

Fagus crenata is the most widely distributed broad-leaved deciduous tree species in cool temperate forests in Japan. Furthermore, virgin natural forests of *F. crenata* in Shirakami Mountains, which are located in northeast Japan, were registered by UNESCO as a World Natural Heritage in December 1993. However, forest decline and dieback of *F. crenata* have recently been observed in several mountainous areas such as Tanzawa Mountains in central Japan (Maruta et al., 1999). It has been suggested that gaseous air pollutants and depositing nitrogen are environmental stresses relating to forest decline of *F. crenata* in Tanzawa Mountains (Maruta et al., 1999; Okochi & Igawa, 2001). To protect *F. crenata* forests in Japan from various environmental stresses, improved knowledge of the growth and physiological responses of this tree species to gaseous air pollutants and depositing nitrogen is required (Izuta et al., 2004;

Yonekura et al., 2001). In the present study, therefore, we investigated the effects of N supply to soil on the sensitivity to O_3 of growth and net photosynthesis of *Fagus crenata* seedlings. This is the first report concerning the combined effects of O_3 and N supply on Japanese or Asian deciduous broad-leaved tree species.

2 Materials and Methods

In March 2004, 2-year-old seedlings of *F. crenata* Blume (Japanese beech) were individually planted in 12 L pots filled with andisol (black soil) collected from a forest floor of deciduous broad-leaved tree species in Maebashi, Gunma Prefecture, Japan. During the experimental period from 16 April to 22 September 2004, 144 seedlings were grown in open-top chambers (OTCs) located at the Akagi Testing Center of the Central Research Institute of Electric Power Industry (Maebashi, Gunma Prefecture, Japan). The whole-plant dry mass, plant height and stem base diameter of the seedlings at the beginning of the experiment were $3.59 \pm 3.12 \text{ g}$, $18.9 \pm 0.2 \text{ cm}$ and $5.9 \pm 0.1 \text{ mm}$, respectively.

From April to September 2004, three different amounts of N were added monthly as NH_4NO_3 solution to the potted soil. The total N loads were 0, 20 and $50 \text{ kg ha}^{-1} \text{ year}^{-1}$ on the basis of potted soil surface area, these soil treatments being designated as N0, N20 and N50, respectively. During the experimental period, the seedlings were exposed to charcoal-filtered air (CF) with O_3 at $<15 \text{ nl l}^{-1}$ (ppb) or O_3 at 1.0, 1.5 and 2.0 times the ambient concentration. Three replicated open-top chambers were randomly assigned to each gas treatment. The AOT40 during the daylight hours with a solar irradiation of $>50 \text{ W m}^{-2}$ in the CF, 1.0, 1.5 and 2.0 times ambient O_3 treatments during the experimental period were 0.6, 29, 64 and $104 \mu\text{l l}^{-1} \text{ h}$ (ppm h), respectively. On 23 September 2004, all the seedlings were harvested to measure the leaf area and dry mass of plant organs.

The experiment was of split-plot factorial design with the randomized blocks method. The whole-plot treatment comprised four levels of O_3 replicated three times for a total of 12 OTCs to analyze the data including the variance among the 12 OTCs. The

sub-plot treatment consisted of three levels of N supply to potted soil in each chamber. Four seedlings per OTC were assigned to each gas – N supply – chamber combination.

Soil solution was taken from the potted soil using a soil moisture sampler (Eijkelkamp, The Netherlands) on 1 July 2004. The pH of soil solutions taken from the soil supplied with N at 0, 20 or 50 kg ha⁻¹ year⁻¹ was 5.71, 5.64 or 5.45, respectively.

Gas exchange rates of the first-flush leaves were measured on 30 June 2004 using an infrared gas analyzer system (LI-6400, Li-Cor Inc., USA). Net photosynthetic rate (A_{380}) was determined at $24 \pm 0.1^\circ\text{C}$, $380 \mu\text{mol mol}^{-1} \text{CO}_2$ and a photosynthetically active photon flux density (PPFD) of $1,500 \mu\text{mol m}^{-2} \text{s}^{-1}$. Photosynthetic responses to intercellular CO_2 concentration (C_i) were examined by varying atmospheric CO_2 concentrations of 2–5, 50 and $100 \mu\text{mol mol}^{-1} \text{CO}_2$ in the leaf chamber under a PPFD of $1,500 \mu\text{mol m}^{-2} \text{s}^{-1}$. Carboxylation efficiency (CE) of photosynthesis was determined as the slope of regression line describing photosynthetic responses to C_i .

The concentrations of total soluble protein (TSP) and ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) in the leaves were measured on 16 July 2004. The fresh first-flush leaves (150 mg) were

frozen in liquid nitrogen and homogenized with 1.5 ml extraction buffer containing 100 mM HEPES-KOH (pH 8.0), 5 mM EDTA, 1 mM PMSF, 2% (w/v) PVPP, 0.7% (w/v) polyethylene glycol 20,000, 1% (w/v) Tween 80 and 24 mM 2-mercaptoethanol. The homogenate was centrifuged at 16,000 g for 10 min, and the supernatant was used in the assays of concentrations of TSP and Rubisco by the methods of Nakaji, Fukami, Dokiya, and Izuta (2001).

The concentration of amino acids in the leaves was measured on 2 August 2004. The fresh first-flush leaves (300 mg) were frozen in liquid nitrogen and homogenized with 1.5 ml of 0.6 M HClO_4 . The homogenate was centrifuged at 20,000 g for 20 min, and the supernatant was filtered with 0.2 μm filter (Millex-LG, Millipore Co., Japan). The concentrations of amino acids in the filtrate were analyzed with an automatic amino acid analyzer (Amino Acid Analyzer L-8800, Hitachi Co., Japan).

Statistical analyses of variance were performed with the SPSS[®] statistical package. Analysis of variance (ANOVA) was used to test the effects of O_3 and N supply on the leaf area, plant dry mass, photosynthetic parameters and amino acid concentrations of the seedlings.

Table 1 Effects of O_3 and/or N supply to soil on the leaf area per plant and dry mass (DM) of *Fagus crenata* seedlings on 23 September 2004

Gas treatment	N supply (kg ha ⁻¹ year ⁻¹)	Leaf area (cm ²)	Leaf DM (g)	Stem DM (g)	Root DM (g)	Whole-plant DM (g)
CF	0	344 (152)	2.70 (0.92)	7.15 (0.68)	8.82 (0.67)	19.3 (1.8)
1.0× O_3	0	305 (66)	2.28 (0.68)	6.89 (0.74)	8.36 (0.71)	18.2 (1.5)
1.5× O_3	0	282 (120)	2.25 (0.91)	5.96 (1.33)	7.19 (0.24)	15.9 (2.4)
2.0× O_3	0	296 (40)	2.22 (0.20)	5.93 (0.51)	5.70 (0.87)	14.3 (1.4)
CF	20	335 (66)	2.52 (0.55)	7.78 (1.20)	8.23 (1.26)	19.1 (2.1)
1.0× O_3	20	288 (56)	2.03 (0.40)	7.07 (1.53)	7.79 (0.17)	17.6 (1.8)
1.5× O_3	20	369 (14)	2.60 (0.24)	6.25 (1.15)	7.07 (0.87)	16.4 (2.2)
2.0× O_3	20	323 (98)	2.26 (0.70)	5.69 (0.62)	5.88 (0.09)	14.3 (1.4)
CF	50	297 (34)	2.17 (0.28)	6.92 (0.77)	8.69 (0.79)	18.5 (1.6)
1.0× O_3	50	379 (118)	2.89 (0.99)	7.76 (2.01)	7.59 (0.94)	18.8 (4.0)
1.5× O_3	50	367 (57)	2.75 (0.58)	6.71 (0.77)	6.73 (0.60)	16.7 (0.7)
2.0× O_3	50	317 (70)	2.15 (0.59)	5.59 (1.14)	5.48 (0.77)	13.6 (2.4)
ANOVA ^a	O_3	ns	ns	**	***	***
	N	ns	ns	ns	ns	ns
	$\text{O}_3 \times \text{N}$	ns	ns	ns	ns	ns

Each value shows the mean of three independent chamber replicates, and the standard deviation is indicated in parenthesis.

^aTwo-way ANOVA: ** $p < 0.01$, *** $p < 0.001$, ns=not significant.

Table 2 Effects of O₃ and/or N supply to soil on the net photosynthetic rate at 380 $\mu\text{mol mol}^{-1}$ CO₂ (A_{380}), carboxylation efficiency (CE) on 30 June 2004, and the concentrations of ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) and total soluble protein (TSP) on 16 July 2004 in the leaves of *Fagus crenata* seedlings

Gas treatment	N supply (kg ha ⁻¹ year ⁻¹)	A_{380} ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	CE (mol m ⁻² s ⁻¹)	Rubisco (mg g FW ⁻¹)	TSP (mg g FW ⁻¹)
CF	0	10.53 (0.33)	0.0357 (0.0028)	9.87 (1.64)	27.5 (2.4)
1.0×O ₃	0	9.39 (0.42)	0.0321 (0.0013)	9.26 (1.85)	25.2 (1.5)
1.5×O ₃	0	8.42 (0.71)	0.0305 (0.0040)	7.99 (0.58)	23.6 (2.2)
2.0×O ₃	0	5.22 (0.79)	0.0214 (0.0019)	5.91 (0.84)	20.9 (1.6)
CF	20	11.62 (0.64)	0.0407 (0.0016)	10.67 (1.37)	28.5 (4.0)
1.0×O ₃	20	10.14 (0.07)	0.0364 (0.0032)	10.25 (1.67)	27.4 (2.7)
1.5×O ₃	20	7.32 (1.89)	0.0313 (0.0034)	10.71 (0.58)	23.6 (1.3)
2.0×O ₃	20	6.11 (0.14)	0.0248 (0.0011)	7.54 (1.40)	24.2 (3.3)
CF	50	10.29 (0.16)	0.0391 (0.0026)	10.03 (0.37)	29.0 (3.4)
1.0×O ₃	50	9.78 (1.48)	0.0395 (0.0007)	9.70 (0.13)	26.3 (3.4)
1.5×O ₃	50	7.70 (1.45)	0.0269 (0.0040)	7.88 (1.88)	23.7 (1.3)
2.0×O ₃	50	6.90 (0.41)	0.0270 (0.0021)	7.09 (0.86)	22.5 (1.5)
ANOVA ^a	O ₃	***	***	**	*
	N	ns	*	*	ns
	O ₃ ×N	ns	ns	ns	ns

Each value shows the mean of three independent chamber replicates, and the standard deviation is indicated in parenthesis.

^a Two-way ANOVA: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, ns = not significant.

Table 3 Effects of O₃ and/or N supply to soil on the acidic, basic, uncharged polar, nonpolar and total amino acid concentrations in the leaves of *Fagus crenata* seedlings on 2 August 2004

Gas treatment	N supply (kg ha ⁻¹ year ⁻¹)	Acidic ^a (nmol g FW ⁻¹)	Basic ^b (nmol g FW ⁻¹)	Uncharged polar ^c (nmol g FW ⁻¹)	Nonpolar ^d (nmol g FW ⁻¹)	Total ^e (nmol g FW ⁻¹)
CF	0	879 (348)	87 (3)	385 (75)	964 (241)	2,316 (320)
1.0×O ₃	0	1,223 (39)	109 (20)	508 (50)	1,075 (114)	2,915 (116)
1.5×O ₃	0	1,315 (114)	67 (24)	447 (98)	864 (335)	2,693 (501)
2.0×O ₃	0	1,339 (394)	131 (113)	496 (93)	528 (137)	2,494 (372)
CF	20	862 (382)	115 (51)	507 (45)	1,282 (139)	2,766 (206)
1.0×O ₃	20	1,175 (49)	124 (70)	462 (37)	886 (132)	2,647 (136)
1.5×O ₃	20	1,256 (173)	104 (45)	496 (46)	752 (157)	2,608 (316)
2.0×O ₃	20	1,417 (114)	91 (25)	577 (106)	625 (161)	2,709 (176)
CF	50	971 (258)	89 (32)	465 (60)	1,112 (217)	2,637 (162)
1.0×O ₃	50	1,390 (367)	164 (84)	557 (59)	1,368 (197)	3,479 (580)
1.5×O ₃	50	1,338 (173)	130 (45)	517 (96)	866 (141)	2,850 (145)
2.0×O ₃	50	1,468 (316)	111 (49)	540 (152)	700 (37)	2,819 (416)
ANOVA ^f	O ₃	*	ns	ns	**	ns
	N	ns	ns	ns	ns	*
	O ₃ ×N	ns	ns	ns	ns	ns

Each value shows the mean of three independent chamber replicates, and the standard deviation is indicated in parenthesis.

^a Acidic amino acid; aspartate and glutamate

^b Basic amino acid; lysine, arginine and histidine

^c Uncharged polar amino acid; glycine, serine, threonine and glutamine

^d Nonpolar amino acid; alanine, valine, leucine, isoleucine and phenylalanine

^e Total amino acid

^f Two-way ANOVA: * $p < 0.05$, ** $p < 0.01$, ns=not significant.

3 Results

Table 1 shows the effects of O₃ and/or N supply to the soil on the growth parameters of *F. crenata* seedlings. The exposure of the seedlings to O₃ significantly reduced the stem, root and whole-plant dry mass. The N supply did not significantly change the leaf area per plant nor the leaf, stem, root and whole-plant dry mass. No significant interactive effects of O₃ and N supply on the leaf area per plant and leaf, stem, root and whole-plant dry mass were detected.

Table 2 indicates the effects of O₃ and/or N supply to the soil on the photosynthetic parameters and the concentrations of Rubisco and TSP in the leaves of *F. crenata* seedlings. The O₃ significantly reduced the A₃₈₀, CE and concentrations of Rubisco and TSP in the leaves of the seedlings. The N supply significantly increased the CE and Rubisco concentration. No significant interactive effects of O₃ and N supply on the A₃₈₀, CE and concentrations of TSP and Rubisco were found.

Table 3 shows the effects of O₃ and/or N supply to the soil on the concentrations of amino acids in the leaves of *F. crenata* seedlings. The O₃ significantly increased the concentration of acidic amino acid and significantly reduced the concentration of nonpolar amino acid in the leaves of the seedlings. The N supply significantly increased the total amino acid concentration. No significant interactive effects of O₃ and N supply to the soil on the acidic, basic, uncharged polar, nonpolar and total amino acid concentrations were detected.

4 Discussion

In the present study, the exposure to O₃ adversely affected the growth and photosynthetic parameters of *F. crenata* seedlings. Ozone reduces the growth of European and North American forest tree species with an acceleration of leaf loss (Pääkkönen & Holopainen, 1995; Pell, Sinn, & Johansen, 1995). In the present study, however, leaf loss of *F. crenata* seedlings was not accelerated by the exposure to O₃ (data not shown). Therefore, O₃-induced reduction in the growth of the seedlings was considered to be mainly due to the reduction in net photosynthetic rate (Yonekura et al., 2001). When net photosynthetic rate

was significantly reduced by O₃, this gas also caused significant reduction in the concentration of Rubisco in the leaves of the seedlings. The O₃-induced reduction in the concentration of Rubisco is primarily caused by enhanced degradation of leaf proteins, and Rubisco is remobilized more rapidly than the other proteins during the leaf senescence (Brendley & Pell, 1998; Delrot, Rochat, Tegeder, & Frommer, 2001). In the present study, O₃ significantly reduced the concentrations of TSP and Rubisco with an increase of acidic amino acid concentration in the leaves of *F. crenata* seedlings. The acidic amino acids, glutamate and aspartate, are necessary to synthesize glutamine and asparagine which are important amino acids for nitrogen remobilization in plants (Delrot et al., 2001). Therefore, O₃ accelerated physiological senescence with the degradation of protein such as Rubisco in the leaves of *F. crenata* seedlings.

Although N supply to the soil at $\leq 50 \text{ kg ha}^{-1} \text{ year}^{-1}$ significantly increased the CE and concentrations of Rubisco and total amino acid in the leaves of *F. crenata* seedlings, the whole-plant dry mass and net photosynthetic rate were not significantly changed by the N supply. Therefore, the effects of N supply at $\leq 50 \text{ kg ha}^{-1} \text{ year}^{-1}$ on the growth and net photosynthesis of the seedlings are considered to be relatively small at least during one growing season.

No significant interactive effects of O₃ and N supply to the soil on the growth, photosynthetic parameters and leaf amino acid concentrations of *F. crenata* seedlings were detected. This indicates that the combined effects of O₃ and N supply are additive on the growth and net photosynthesis of the seedlings. Pääkkönen and Holopainen (1995) reported that a sufficient N supply induced greater resistance to O₃ of *Betula pendula* seedlings. In *Populus tremuloides* seedlings, on the contrary, the degree of O₃-induced reduction in the biomass was lower under relatively low N supply conditions (Pell et al., 1995). These contrastive results indicate that the effects of N supply on the sensitivity to O₃ are quite different between Japanese and European or American deciduous broad-leaved tree species. Therefore, it is necessary to evaluate critical levels of O₃ for protecting Japanese forest ecosystems based on the interspecific difference in the sensitivity to O₃ under different N loads among deciduous broad-leaved tree species.

In conclusion, N supply to the soil at $\leq 50 \text{ kg ha}^{-1} \text{ year}^{-1}$ does not significantly affect the sensitivity to

O₃ of growth and net photosynthesis of *F. crenata* seedlings.

Acknowledgements This research was funded by a grant from Ministry of the Environment, Japan (Global Environment Research Fund). The authors are greatly indebted to Prof. Hisao Itabashi and Prof. Keiji Hasumi of Tokyo University of Agriculture and Technology for their invaluable advice on the analysis of amino acid.

References

- Brendley, B. W., & Pell, E. J. (1998). Ozone-induced changes in biosynthesis of Rubisco and associated compensation to stress in foliage of hybrid poplar. *Tree Physiology*, 18, 81–90.
- Bytnerowicz, A., Godzik, B., Grodzinska, K., Fraczek, W., Musselman, R., Manning, W., et al. (2004). Ambient ozone in forests of the central and eastern European mountains. *Environmental Pollution*, 130, 5–16.
- Chappelka, A. H., & Samuelson, L. J. (1998). Ambient ozone effects on forest trees of the eastern United States: A review. *New Phytologist*, 139, 91–108.
- Delrot, S., Rochat, C., Tegeder, M., & Frommer, W. B. (2001). *Plant nitrogen*. Paris: INRA-Springer, pp. 215.
- Derwent, R., Collins, W., Johnson, C., & Stevenson, D. (2002). Global ozone concentrations and regional air quality. *Environmental Science & Technology*, 36, 379–382.
- Izuta, T., Yamaoka, T., Nakaji, T., Yonekura, T., Yokoyama, M., Funada, R., et al. (2004). Growth, net photosynthesis and leaf nutrient status of *Fagus crenata* seedlings grown in brown forest soil acidified with H₂SO₄ or HNO₃ solution. *Trees*, 18, 677–685.
- Maruta, E., Shima, K., Horie, K., Aoki, M., Dokiya, Y., Izuta, T., et al. (1999). Forest decline of *Fagus crenata* at Mt. Hinokiboramaru (Tanzawa, Kanagawa Prefecture, Japan) and acid deposition (in Japanese). *Environmental Sciences (Japan)*, 12, 241–250.
- Ministry of the Environment (2004). *Summary report of research results under the GERF (Global Environment Research Fund) in FY2003*. Japan: Ministry of the Environment, pp. 238.
- Nakaji, T., Fukami, M., Dokiya, Y., & Izuta, T. (2001). Effects of high nitrogen load on growth, photosynthesis and nutrient status of *Cryptomeria japonica* and *Pinus densiflora* seedlings. *Trees*, 15, 453–461.
- Nihlgård, B. (1985). The ammonium hypothesis – an additional explanation to the forest dieback in Europe. *Ambio* 14, 2–8.
- Okochi, H., & Igawa, M. (2001). Elevational patterns of acid deposition into a forest and nitrogen saturation on Mt. Oyama, Japan. *Water, Air, and Soil Pollution*, 130, 1091–1096.
- Pääkkönen, E., & Holopainen, T. (1995). Influence of nitrogen supply on the response of clones of birch (*Betula pendula* Roth.) to ozone. *New Phytologist*, 129, 595–603.
- Pell, E. J., Sinn, J. P., & Johansen, V. (1995). Nitrogen supply as a limiting factor determining the sensitivity of *Populus tremuloides* Michx. to ozone stress. *New Phytologist*, 130, 437–446.
- Vingarzan, R. (2004). A review of surface ozone background levels and trends. *Atmospheric Environment*, 38, 3431–3442.
- Wright, R. F., Brandrud, T.-E., Clemensson-Lindell, A., Hultberg, H., Kjønås, O. J., Moldan, F., et al. (1995). NITREX Project: Ecosystem response to chronic additions of nitrogen to a spruce-forested catchment at Gårdsjön, Sweden. *Ecological Bulletins*, 44, 322–334.
- Yonekura, T., Honda, Y., Oksanen, E., Yoshidome, M., Watanabe, M., Funada, R., et al. (2001). The influences of ozone and soil water stress, singly and in combination, on leaf gas exchange rates, leaf ultrastructural characteristics and annual ring width of *Fagus crenata* seedlings. *Journal of Japan Society for Atmospheric Environment*, 36, 333–352.

Stem Growth of *Picea Abies* in South Western Sweden in the 10 Years Following Liming and Addition of PK and N

Ulf Sikström

Received: 13 June 2005 / Accepted: 4 March 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Liming and/or application of specific nutrients have been proposed as countermeasures to the acidification of forest soils in southern Sweden. In this study the stem growth of *Picea abies* (L.) Karst. growing on acidic mineral soils in SW Sweden was investigated 10 years after additions of lime (Ca; 3000 kg lime ha⁻¹), lime plus P (25 kg ha⁻¹) and K (80 kg ha⁻¹), or N in low doses (2 × 10 kg ha⁻¹ yr⁻¹) (treatments: CaPK, Ca, N, CaPKN, and 2Ca2P2K, respectively). Compared with the control, stem growth was increased following all treatments involving lime additions, including liming alone. The PK addition did not seem to affect growth. The most plausible cause of the observed growth increases was that the lime additions indirectly increased the supply of plant-available N. The annual low-dose N addition did not significantly affect growth. This suggests that air-borne deposition of N, which supplies very small doses of N throughout the year, has a minor or even negligible influence on *P. abies* growth.

Keywords ammonium nitrate · calcite · dolomite · forest production · Norway spruce · phosphorous · potassium

1 Introduction

Southern Sweden has been subjected to substantial deposition of S and N air pollutants for several decades, amounting to 15–25 kg ha⁻¹ yr⁻¹ of both elements (Lövsblad, Kindbom, Grennfeldt, Hultberg, & Westling, 1995). The deposited S- and N-containing compounds contribute to the acidification observed in forest soils in the area (Nilsson, 1993; Nilsson & Tyler, 1995). From the mid-1980s to date, the N-deposition has been more or less constant, whereas the S-deposition has been substantially reduced (Uggla, Hallgren-Larsson, & Malm, 2004). Modelling studies have suggested that the reduction in S-deposition will lead to improved surface water quality, but the reversal of soil acidification will be slow in many cases in southern Sweden (Moldan, 1999, Sverdrup et al., 2005). In order to accelerate the reversal, the National Board of Forestry in Sweden has proposed an action plan for liming, possibly admixed with ashes to include nutrients such as P and K, of several hundred thousands hectares of forest soils (Anon., 2001). For forest sites in the most acidified parts of southern Sweden, relevant knowledge of tree-growth responses to combined treatments with lime and nutrients is limited or even non-existent. Generally, data on the long-term effects on tree growth of both liming and combined treatments are lacking.

Deposited N may acidify the soil, although it may also promote tree growth. However, the effects of

U. Sikström (✉)
Skogforsk (The Forestry Research Institute of Sweden),
Uppsala Science Park,
SE-751 83 Uppsala, Sweden
e-mail: ulf.sikstrom@skogforsk.se

deposited air-borne N pollutants on tree growth are unclear, and conflicting conclusions have been drawn (cf. Elfving & Tegnhammar, 1996; Eriksson & Johansson, 1993; Nadelhoffer et al., 1999; Sikström, 2002).

To help clarify the issues outlined above an experimental series was established in the early 1990s in a number of *Picea abies* (L.) Karst. stands in south-western Sweden. The tested treatments included additions of lime, lime plus P and K, and addition of N in low annual doses. Five years after the treatments, there were no clear effects on stem growth, except for a tendency for growth to increase after CaPKN addition (Sikström, 2002). In the study reported here, the 10-year effects on stem growth were evaluated. The 10-year evaluation mainly followed the previously applied procedures (Sikström, 2002). However, a major difference was that only three of the four original experimental sites could be examined, since one of the experimental stands had been harvested in the intervening period at the request of the land owner.

2 Materials and Methods

2.1 Experimental Sites and Design

The three experimental sites examined were established in SW Sweden in 1991, Site 244 Åled (56° 46' N, 12° 56' E) or 1992, Sites 246 Brekille (56° 15' N, 13° 06' E) and 247 Össjö (56° 14' N, 13° 04' E). The

region where the sites are located has an annual precipitation of 800–1000 mm and a mean annual temperature of 7–8°C (Alexandersson, Karlström, & Larsson-McCann, 1991). Several other characteristics of each experimental site (location, atmospheric deposition, field-layer composition, stand type, soil chemistry, soil-water chemistry and site history) were reported by Nohrstedt (2001) and Sikström (2002).

A randomised block design with six treatments (Table 1) was used at all sites; three blocks at Site 244, and two blocks at Sites 246 and 247. The size of the experimental plots was 30 m×30 m. Lime (3,000 kg ha⁻¹ or 6,000 kg ha⁻¹) and PK were applied as single applications at the start of the experimental treatments. The N treatment consisted of annual applications of 20 kg N ha⁻¹, applied as 10 kg ha⁻¹ on two occasions. The treatments started in spring 1992 (Site 244) or spring 1993 (Sites 246 and 247) (see further Sikström, 2002).

2.2 Growth Study

All measurements of tree growth were performed within a circle of 10 m radius located in the centre of each treatment plot. The heights (dm) and diameters (mm; cross-callipered at breast-height) of the sample trees were measured, and increment cores were taken with a borer at breast-height. The procedures applied in this 10-year evaluation followed those used in the 5-year evaluation, which are described in detail in Sikström (2002). However, one difference in the 10-year revision was that fewer trees were present on the

Table 1 Experimental treatments

Element (kg ha ⁻¹)	Treatment					
	0	CaPK ^{a,b}	Ca ^a	N ^c	CaPKN ^{a,b,c}	2Ca2P2K ^{a,b}
Ca	–	1,135	1,100	–	1,135	2,270
P	–	25	–	–	25	50
K	–	79	–	–	79	158
Mg ^d	–	192/128	184/120	–	192/128	384/256
N	–	–	–	10×2×10	10×2×10	–
Cu	–	1.2	–	–	1.2	2.3
S	–	23	–	–	23	46
Cl	–	73	–	–	73	146

^a The lime consisted of a mixture of limestone (CaCO₃) and dolomite [CaMg(CO₃)₂]

^b P and K was applied as “PKCu 7–21”, where P was in the form of superphosphate, and K as potassium chloride

^c N given as NH₄NO₃; 10 kg N ha⁻¹ in May and 10 kg N ha⁻¹ in October in each of 10 consecutive years

^d The first value refers to doses at Site 244 and the latter to doses at Sites 246 and 247

experimental plots, since the stands were thinned in conjunction with the 5-year evaluation. In these thinning operations, the same thinning grade (percentage of basal area removed) was applied to all plots within an experimental block. In the new evaluation of treatment effects, the total growth during the 10 years following the treatments was assessed, i.e. the 10-year growth of the standing trees plus the growth of the thinned trees during the first 5-year period. The effects of the treatments on basal area increment (BAI) and volume increment (VI) of the stems were estimated both for individual sites and for all sites together.

2.3 Statistical Methods

The 10-year BAI and VI values calculated for each plot were subjected to analysis of variance, and a covariate (BAI or VI during 5 years before treatment, as appropriate) was usually included in the model. The following model was used in the analyses of individual sites:

$$y_{jk} = \mu + u_j + t_k + b(g_{jk} - \bar{g}) + e_{jk} \quad (1)$$

where y_{jk} are BAI or VI in plot jk ; μ =overall mean; u_j =effect of block j ($j=1, \dots, 3$ or $1, \dots, 2$); t_k = effect of treatment k ($k=1, \dots, 6$); b is the coefficient for the regression of BAI on BAI_{before} , or VI on VI_{before} ; g is BAI_{before} , or VI_{before} in plot jk ; e_{jk} is the random error, NID $(0, \sigma_e^2)$.

When all sites were included in the analyses, the above model was also used for calculations based on least-square-mean values of the different treatments at individual sites. The only difference was that u_j in the model was substituted by s_i (see below). In an alternative analysis of all sites, based on individual plots, the following model was used:

$$y_{ijk} = \mu + s_i + u_{(i)j} + t_k + st_{ik} + b(g_{(i)jk} - \bar{g}) + e_{(i)jk} \quad (2)$$

where y_{ijk} is BAI or VI in plot ijk ; μ = overall mean; s_i is the effect of site i ($i=1, \dots, 3$); u_j is the effect of block j ($j=1, \dots, 2$ or $1, \dots, 3$); t_k is the effect of treatment k ($k=1, \dots, 6$); st_{ik} is the interaction between site and treatment; b is the coefficient for the regression of BAI on BAI_{before} , or VI on VI_{before} ; g is BAI_{before} or VI_{before} in plot ijk ; and $e_{(i)jk}$ is the

random error, NID $(0, \sigma_e^2)$. This model allows all of the data to be used in the analyses, to test for interactions between site and treatment, while retaining the within-site variation.

The GLM procedure in SAS was used for the statistical analyses (SAS, 1999). The mean square st_{ik} was used as the denominator in the analyses of the effects of treatment (t_k) when the model included more than one site. Differences between individual treatment means were evaluated with Tukey's significant differences (HSD) mean separation test. The effect of PK (i.e., the difference between CaPK and Ca, hereafter called the "PK-effect") was given special attention. The difference $[(CaPK+2Ca2P2K)-(2 \times \text{Control})]$, hereafter called the "CaPK-effect", was also evaluated. Treatment effects were considered to be statistically significant when $p < 0.05$.

In the analyses, the residuals were tested for normality, using the Shapiro–Wilk test (Shapiro & Wilk, 1965). Kurtosis and skewness were also analysed, and the residuals in normal probability plots were visually interpreted. Based on these analyses, it was concluded that data not had to be transformed.

3 Results

The mean stem-volume growth on the control plots was 11.3, 18.9, and 24.5 $\text{m}^3 \text{ha}^{-1} \text{yr}^{-1}$ at Sites 244, 246, and 247, respectively, during the 10-year period following the treatments (Table 2). When all sites were analysed together, treatments CaPKN and 2Ca2P2K showed significantly higher growth than the control, by 29% for BAI and 23–30% for VI ($p < 0.05$). These treatments also resulted in higher growth than the N treatment; 17–18% and 14–18% higher BAI ($p < 0.08$) and VI ($p < 0.05$), respectively. In addition, VI following these treatments tended ($p < 0.10$) to be higher (by 9–14%) than following the Ca treatment. Compared with the control, the CaPK treatment resulted in 20% higher BAI ($p < 0.06$) and 17–19% higher VI ($p < 0.05$), while the Ca treatment gave 13% higher VI ($p < 0.06$).

There were statistically significant "CaPK-effects" for both BAI and VI ($p = 0.002$ – 0.004) in the analyses of all sites. For individual sites, the "CaPK-effect" was always significant for BAI ($p = 0.002$ – 0.048), but not always for VI ($p = 0.020$ – 0.201). No "PK-effect" was detected in any case.

Table 2 Basal area ($\text{m}^2 \text{ ha}^{-1} \text{ yr}^{-1}$) and volume ($\text{m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$) increments during the 10 years following each treatment at each experimental site and for all sites analysed together

Experiment	Treatment						<i>p</i> -value, treatment
	0	CaPK	Ca	N	CaPKN	2Ca2P2K	
Basal area increment							
244 (<i>n</i> =3)	0.674a (0.044)	0.850a (0.043)	0.732a (0.045)	0.693a (0.045)	0.901b (0.047)	0.862a (0.043)	0.021
246 (<i>n</i> =2)	1.31a (0.060)	1.73b (0.050)	1.57ab (0.051)	1.55ab (0.052)	1.84b (0.057)	1.70b (0.052)	0.048
247 (<i>n</i> =2)	1.74a (0.039)	1.88ab (0.037)	2.02bc (0.036)	1.85ab (0.038)	2.06bc (0.038)	2.23c (0.036)	0.005
All sites (lsmeans)	1.24a (0.052)	1.49ab (0.052)	1.44ab (0.052)	1.36ab (0.052)	1.60b (0.052)	1.60b (0.052)	0.004
All sites (plots ¹)	1.19a (0.056)	1.43ab (0.052)	1.38ab (0.050)	1.31ab (0.057)	1.53b (0.056)	1.53b (0.054)	0.004
Volume increment							
244 (<i>n</i> =3)	11.3 (1.02)	14.2 (1.00)	12.5 (1.06)	12.0 (1.06)	14.8 (1.06)	13.7 (1.03)	0.20
246 (<i>n</i> =2)	18.9a (0.54)	23.7bc (0.48)	21.7ab (0.48)	21.4ab (0.48)	25.1c (0.53)	24.1bc (0.49)	0.020
247 (<i>n</i> =2)	24.5 (0.98)	26.9 (0.95)	27.7 (1.0)	26.3 (0.95)	29.8 (1.0)	30.1 (0.95)	0.085
All sites (lsmeans)	18.1a (0.50)	21.6bcd (0.50)	20.5ab (0.50)	20.0ab (0.50)	23.5d (0.50)	22.7cd (0.50)	0.000
All sites (plots)	18.0a (0.46)	21.1bcd (0.44)	20.3bc (0.44)	19.4ab (0.44)	22.6d (0.46)	22.1cd (0.45)	0.000

Except for “All sites/Lsmeans”, all values (least square means) were corrected using covariates based on the basal area growth and volume growth (as appropriate) at the respective sites during the 5 years before the treatments. Values in the same row marked with different letters differ significantly ($p < 0.05$). Figures within brackets denote 1 SE

¹ There was a significant site $\times$ treatment interaction ($p = 0.005$)

For Sites 244 and 246, similar rankings of treatment-mean-growth rates were found for both BAI and VI ($0 < \text{N} < \text{Ca} < \text{CaPK}$, $2\text{Ca}2\text{P}2\text{K} < \text{CaPKN}$), but the rankings were somewhat different for site 247 (Table 2). Compared with the control, statistically significant effects or tendencies were found at all individual sites for BAI after addition of CaPKN and 2Ca2P2K, addition of CaPK at Site 246, and addition of Ca at site 247. For VI, similar treatment effects were detected only at Site 246 (Table 2). Other significant treatment effects ($p < 0.05$), according to pair-wise comparison at individual sites, were $2\text{Ca}2\text{P}2\text{K} > \text{CaPK}$ and N (for BAI at Site 247) and $\text{CaPKN} > \text{Ca}$ and N (for VI at Site 246).

Averaged over the seven blocks, the mean annual BAI for all treatments including lime (i.e. except treatment N), increased slightly relative to the control during the next c. 8 years (Fig. 1). Thereafter, the annual relative growth seemed to change to a more constant level, although it was still 20–40% higher than the control 10 years after treatment. The average relative growth rates, for each treatment, were quite similar at the individual sites (244, 246 and 247).

4 Discussion

The previously observed tendency for CaPKN addition to increase growth in the 5 years following the

treatment (Sikström, 2002) had strengthened at this re-evaluation covering a 10-year effect period. For this 10-year period significant increases (20–25% compared with the control) in growth were found for all treatments including lime and PK. Moreover, liming alone resulted in a c. 15% increase in growth. The mean growth was also 10% higher after N addition, but this difference was not statistically significant.

The short-term-growth response after liming stands of coniferous trees, i.e. during the c. 5–10 years following treatment, is known to be variable (see Sikström, 2001a and references therein), and the response seems to be associated with both soil fertility and the C to N ratio in the humus layer (Sikström, 2001b). On low-productivity (high C/N) sites growth will usually be somewhat reduced by liming, on moderately-productive sites it will be unaffected, and growth tends to increase on fertile (low C/N) sites (Sikström, 2001b). The present results from sites 244, 246 and 247, representing quite fertile sites, are consistent with this general pattern of growth responses of coniferous trees to liming.

At the present experimental sites, the treatments including lime were associated with the most marked changes in many of the documented soil properties 4 years after treatment (Nohrstedt, 2001). In the O-horizon, liming raised the pH by 0.6–1 units, the

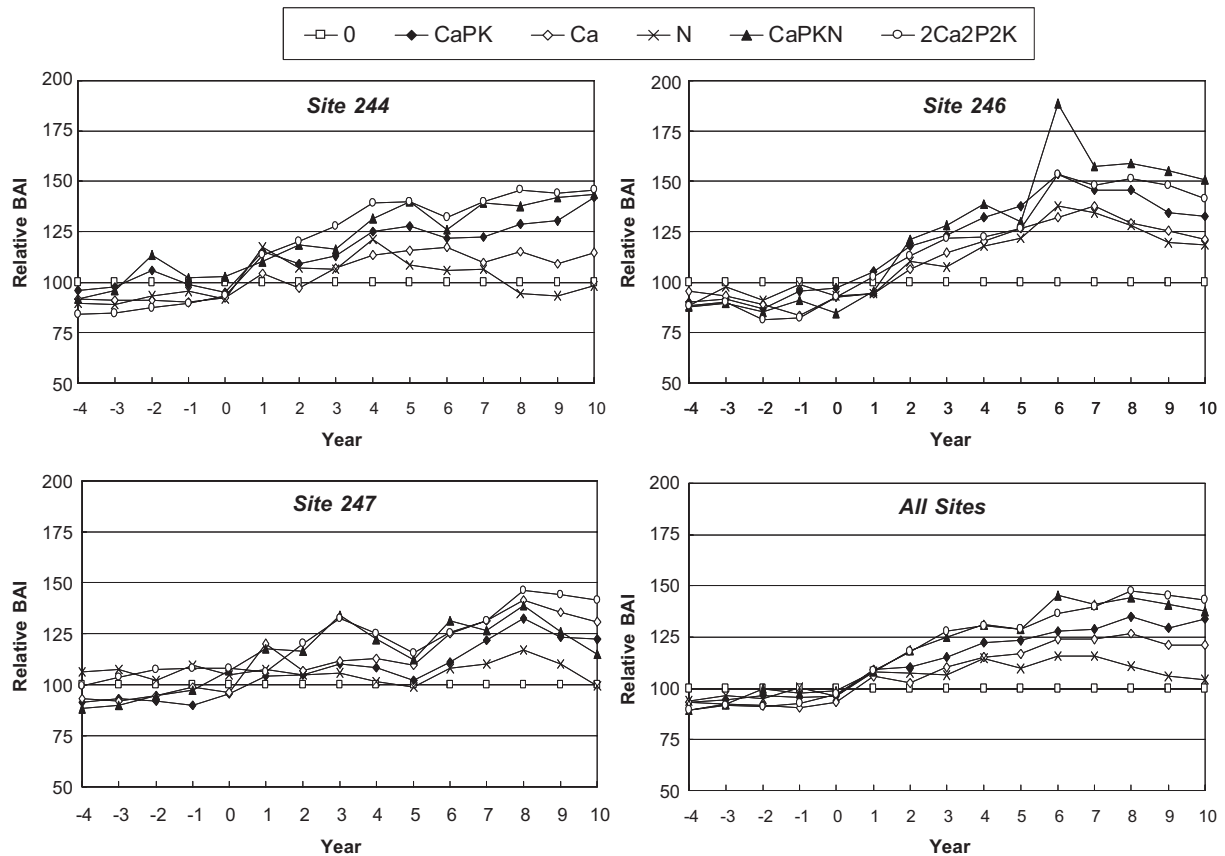


Fig. 1 Annual relative basal area increment (BAI, %) for each of the treatment plots (t) in relation to untreated control plots (c, 100%), five years before (b) and ten years after (a) treatment: means for three (Site 244), two (Sites 246 and 247) and seven (All Sites) replicates. The post-treatment values (years 1–10) were adjusted for pre-treatment growth rates, i.e. by the ratio

between the growth rates on the treated plots and the control plots during the five year period prior to treatment $[(\text{annual BAI}_{t,a} / \text{annual BAI}_{c,a}) / (5 \text{ yr BAI}_{t,b} / 5 \text{ yr BAI}_{c,b})]$. This was done for each treatment individually within all replicates (blocks). Explanations: t = treated plot; c = control plot; a = after treatment; b = before treatment

potential net N mineralization rate was approximately doubled, and potential nitrification was increased several-fold, indicating that liming increased the turnover of N and, potentially, the supply of plant-available N. Increased net N mineralization in the O-horizon is commonly observed after liming fertile forest soils (Persson, Wirén, Andersson, 1990/91; Smallidge, Brach, Mackun, 1993; Kreutzer, 1995). Thus, increased N availability in the soil is a plausible cause of the observed increase in growth after liming.

In the region where the sites are located, PK addition, at least alone, has not shown any major influence on stem growth of either *P. abies* or *Pinus sylvestris* growing on mineral soils (cf. Sikström, 2002). However, simultaneous application of N and P has sometimes induced stronger growth of *P. abies*

than N alone (Kukkola & Saramäki, 1983; Tamm, 1985).

In the same region, stem growth of both the native conifers usually increases after application of larger single doses of inorganic N than those applied in this study, although there have been exceptions, especially on the most productive sites (cf. Sikström, 2002). Similar to the findings from the first evaluation (Sikström, 2002), data from the current study suggest that the direct fertilization effects on stem growth of annual low-dose N additions may be minor, and consistent with those reported by Nadelhoffer et al. (1999) (see Sikström, 2002, for further details). Thus, N deposition in small pulses throughout the year can be assumed to make minor contributions to increases in tree growth, at least as a direct effect (cf. Nadelhoffer et al., 1999).

At the end of the monitored response period (in 1998) at Sites 244 and 246, the plots treated with lime were affected by wild boars grubbing about in the top soil, which might have influenced the growth responses. However, no marked changes in the annual growth responses (Fig. 1) were generally detected then. One exception is the extreme increase in relative growth in treatment CaPKN at site 246 in the year 1998 (year 6 in Fig. 1), which might have been due to the activity of the wild boars increasing soil turnover, and thus improving growth conditions.

In conclusion, elevated N availability, as an indirect effect of the liming, was the most likely principal cause of the observed increases in stem growth following liming alone and the combined addition of lime and PK. The PK application, and the low-dose N addition alone, seemed to have little or no influence on growth.

Acknowledgements Hagos Lundström and Sten Nordlund performed excellent fieldwork.

References

- Alexandersson, H., Karlström, C., & Larsson-McCann, S. (1991). Temperature and precipitation in Sweden 1961–1990-Reference normals. Swedish Meteorological and Hydrological Institute, Norrköping, Meteorologi no. 81. 88 pp. (in Swedish with English abstract).
- Anon. (2001) Åtgärder mot markförsurning och för ett uthålligt brukande av skogsmarken. Skogsstyrelsen, Meddelande No. 4. 37 pp. Skogsstyrelsens förlag. Jönköping. ISSN 1100-0295. (in Swedish).
- Elfving, B., & Tegnhammar, L. (1996). Trends of growth in Swedish forests 1953–1992: An analysis based on sample trees from National forest inventory. *Scandinavian Journal of Forest Research*, 11, 26–37.
- Eriksson, H., & Johansson, U. (1993). Yields of Norway spruce [*Picea abies* (L.) Karst.] in two consecutive rotations in southwestern Sweden. *Plant Soil*, 154, 239–247.
- Kreutzer, K. (1995). Effects of forest liming on soil processes. *Plant Soil*, 168–169, 447–470.
- Kukkola, M., & Saramäki, J. (1983) Growth response in repeatedly fertilized pine and spruce stands on mineral soils. *Comm. Inst. For. Fenn.*, 114, Helsinki. 55 pp.
- Lövblad, G., Kindbom, K., Grennfeldt, P., Hultberg, H., & Westling, O. (1995). Deposition of acidifying substances in Sweden. In H. Staaf & G. Tyler (Eds.), *Effects of acid deposition and tropospheric ozone on forest ecosystems in Sweden. Ecological Bulletins*, 44, 17–34.
- Moldan, F. (1999). Reversal of soil and water acidification in SW Sweden, simulating the recovery process. PhD Thesis, Acta Universitatis Agriculturae Sueciae, Silvestria 117. SLU, Umeå. 20 pp. plus six appendices. ISBN 91-576-5851-X.
- Nadelhoffer, K. J., Emmett, B. A., Gundersen, P., Kjonaas, O. J., Koopmans, C. J., Schleppi, P. et al. (1999). Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. *Nature*, 398, 145–148.
- Nilsson, S. I. (1993). Acidification of Swedish oligotrophic lakes – Interactions between deposition, forest growth and effects on lake-water quality. *Ambio*, 22, 272–276.
- Nilsson, S. I., & Tyler, G. (1995). Acidification-induced chemical changes of forest soils during recent decades – a review. In H. Staaf & G. Tyler (Eds.), *Effects of acid deposition and tropospheric ozone on forest ecosystems in Sweden. Ecological Bulletins*, 44, 54–64.
- Nohrstedt, H.-Ö. (2001). Effects of liming and fertilization (N, PK) on chemistry and N turnover in acidic forest soils in SW Sweden. *Water, Air, and Soil Pollution*, 139, 343–354.
- Persson, T., Wirén, A., & Andersson, S. (1990/91). Effects of liming on carbon and nitrogen mineralization in coniferous forests. *Water, Air, and Soil Pollution*, 54, 351–364.
- SAS Institute Inc. (1999). *SAS/STAT™, Guide for personal computers, version 8, edition* (pp 3884). Cary, NC: SAS Institute Inc.
- Shapiro, S. S., & Wilk, M. B. (1965). An analysis of variance test for normality (complete samples). *Biometrika*, 52, 591–611.
- Sikström, U. (2001a). Effects of pre-harvest soil acidification, liming and N fertilization on the survival, growth and needle element concentrations of *Picea abies* L. Karst seedlings. *Plant Soil*, 231, 255–266.
- Sikström, U. (2001b). Growth and nutrition of coniferous forests on acidic mineral soils – status and effects of liming and fertilization. PhD Thesis, Acta Universitatis Agriculturae Sueciae, Silvestria 182. SLU Service/Repro, Uppsala. 54 pp. plus five appendices. ISBN 91-576-6066-2.
- Sikström, U. (2002). Effects of liming and fertilization (N, PK) on stem growth, crown transparency, and needle element concentrations of *Picea abies* stands in southwest Sweden. *Canadian Journal of Forest Research*, 32, 1717–1727.
- Smallidge, P. J., Brach, A. R., & Mackun, I. R. (1993). Effects of watershed liming on terrestrial ecosystem processes. *Environmental Review*, 1, 157–171.
- Sverdrup, H., Martinson, L., Alveteg, M., Moldan, F., Kronnäs, V., & Munthe, J. (2005). Modelling recovery of Swedish ecosystems from acidification. *Ambio*, 1, 25–31.
- Tamm, C.-O. (1985). The Swedish optimum nutrition experiments in forest stands – Aims, methods, yield results. *J. Roy. Swe. Acad. Agri. For.*, (Suppl. 17), 9–29. (in Swedish with English summary).
- Uggla, E., Hallgren-Larsson, E., & Malm, G. (2004). Kron-droppsnätet – Tidsutveckling, trendbrott och nationella miljömål. IVL Svenska Miljöinstitutet, Rapport B 1599. 34 pp. (in Swedish).

X-ray Microanalysis of Needles from Douglas Fir Growing in Environments of Contrasting Acidity

Allan G. Sangster · Lewis Ling · Frédéric Gérard ·
Martin J. Hodson

Received: 13 June 2005 / Accepted: 3 April 2006 / Published online: 5 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] shoots from mature trees were collected from two sites of contrasting soil pH: the Glendon campus of York University in Toronto, Canada (pH 6.7 at 40 cm) designated Can.; and Breuil Forest, Morvan, France (pH 4 to 4.5) designated Fr.. Needles were removed from the shoots, frozen in liquid nitrogen, and kept in a cryo-biological storage system prior to X-ray microanalysis on the cold stage (−170°C) of a cryo-SEM. Four elements detected, potassium, phosphorus, sulphur and chlorine, were ubiquitous in the needle tissues from both sites. Manganese was infrequently found in needle tissues from the Fr. site.

Calcium was localized most heavily in the outer tangential wall of the hypodermis and also in the epidermal walls. Silicon (Si) concentrations were higher in the Fr. site than in the Can. site. The epidermis, hypodermis and mesophyll of needles from the Fr. site exhibited the highest Si content, with greater amounts in the tip and middle of the needle than in the base. Aluminium was distributed fairly evenly throughout the tissues, and there were few major sites of concentration.

Keywords Douglas fir · mineral localization · *Pseudotsuga menziesii* · X-ray microanalysis

A. G. Sangster
Division of Natural Sciences, Glendon College,
York University, Toronto,
M4N 3M6, Canada

L. Ling
Department of Earth Sciences, Carleton University,
Ottawa, K1S 5B6, Canada

F. Gérard
Biogéochimie des Ecosystèmes Forestiers, INRA Nancy,
54280 Champenoux, France

M. J. Hodson (✉)
School of Biological and Molecular Sciences,
Oxford Brookes University,
Gipsy Lane, Headington,
Oxford, OX3 0BP, UK
e-mail: mjhodson@brookes.ac.uk

1 Introduction

Douglas fir, *Pseudotsuga menziesii* (Mirb.) Franco, is one of the most important timber-producing trees in the world (Hosie, 1979). For example, it is the main reforestation species in the French Massif Central region (Curt, Lucot, & Bouchard, 2001). Apart from the economic aspect, Douglas fir has considerable ecological significance. It is an integral component of the plant communities found in both the coastal and montane ecozones of the Western Cordillera region (Rocky Mountains) of North America (Farrar, 2004).

Evidence indicates that forest soils in northern Europe and in North America have been significantly acidified by acidic deposition during the last decades (Jentschke et al., 2001). Consequently, studies have

focused on the soil conditions under Douglas fir forests, including soil chemistry (Augusto & Ranger, 2001), hydrology (Gérard, Tinsley, & Mayer, 2004), rooting strategy (Curt et al., 2001), and the activities of ectomycorrhizal fungi in the Douglas fir rhizosphere (Crawford, Floyd, & Li, 2000).

Previous reports of mineral distribution in conifer leaves, as determined by microanalysis, include those for white spruce, eastern white pine, eastern (American) larch, European larch, and balsam fir (Hodson & Sangster, 1998, 2000, 2002; Sangster & Hodson, 2001; Sangster, Hodson, & Huang, 2001). However, information concerning mineral deposition in Douglas fir needles is lacking. The aim of the present work was to determine mineral localization in the needles of Douglas fir, growing at two sites of contrasting soil pH.

2 Site Descriptions

Douglas fir samples were collected in two sites, selected for contrasting soil acidity. The Canadian site (designated Can.), is located in the Forestry Station on the Glendon campus of York University in Toronto, Ontario, Canada. The soil is an alfisol (brown soil) above Palaeozoic strata. Soil pH readings were, at the 3 cm and 40 cm depths, respectively, 6.6

and 6.7. Other details were described previously (Hodson & Sangster, 1998). The French site (designated Fr.) is at Breuil-Chenue forest, Nièvre-Morvan. The soil is an acidic brown soil, with a pH range from 4 to 4.5.

3 Materials and Methods

At both sites, Douglas fir trees were sampled in October, at the end of active uptake and growth. Healthy trees, 18–20 m tall, showing no visible signs of leaf damage were selected for sampling. Branches at a height of approx. 4 m were removed and the branch bases submerged in water during transport to the laboratory. Needles were separated into three cohorts: current (0); current + 1 year old needles (1); and current + 2 year old needles (2). Replicates (ca. 50) of each age cohort were excised from the branches and were maintained in a cryo-biological storage unit (Locator Aid-Barnstead Thermolyne Ltd, Dubuque, Iowa, USA) at the temperature of liquid nitrogen (-196°C) until required.

Frozen needles were prepared for examination following the procedures outlined by Hodson and

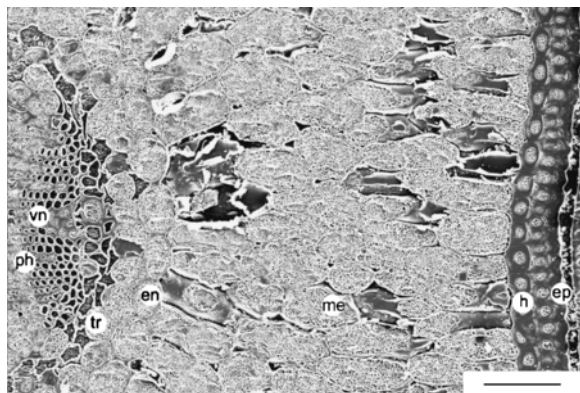


Fig. 1 Internal anatomy of a Douglas fir leaf illustrating the tissues subjected to EDX microanalysis. Surface of the frozen, planed face of a transverse section, 2 mm behind the needle tip; 2 year needle; Can. site. Secondary electron image, cryo-SEM, showing the outer epidermis and hypodermis. Note the extremely thickened cell walls. The mesophyll chlorenchyma tissue extends inwards to the uniseriate endodermis surrounding the vein, consisting of outer transfusion cells, which enclose the vascular tissue. Endodermis (en); epidermis (ep); hypodermis (h); mesophyll (me); phloem (ph); transfusion cells (tr); vein (vn). Scale bar=50 μm

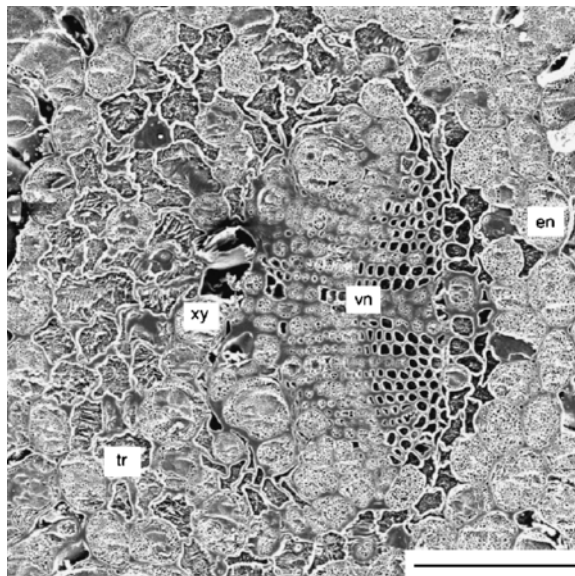


Fig. 2 Anatomy of the Douglas fir leaf; tissues of the central region around the vascular bundle consisting of rows of secondary phloem to the right and xylem to the left. Endodermal cells surround the vein. Secondary electron image; cryo-SEM; transverse section 2 mm from tip, 2 year needle, Can. site. Xylem (xy); other abbreviations as in Fig. 1. Scale bar=100 μm

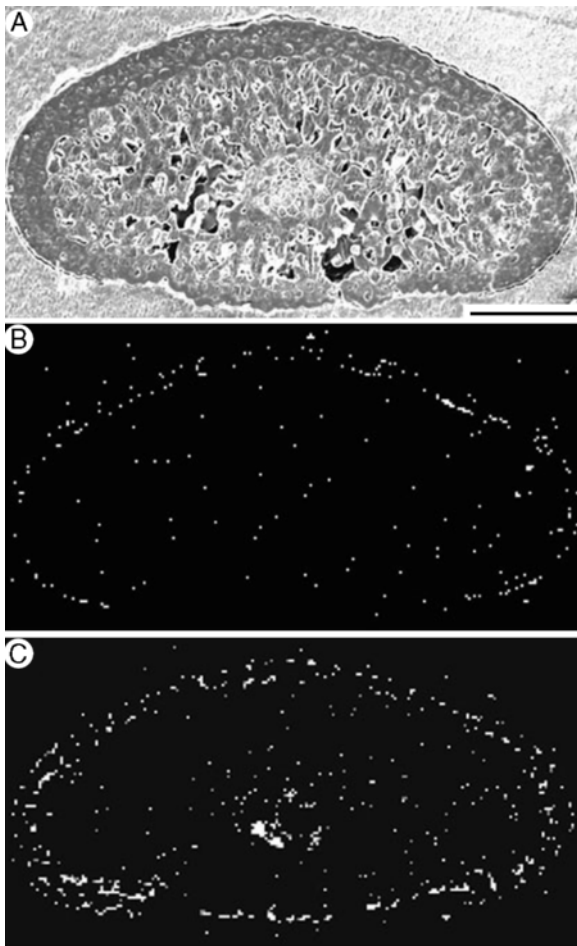


Fig. 3 EDX microanalysis of a cryo-SEM transverse section of a Douglas fir needle, tip region, 2 year needle, (Can.) site. **A**, Secondary electron image; entire needle. Scale bar=100 μm . **B**, Matching Ca X-ray distribution image for **A**. **C**, Matching Si X-ray distribution image for **A**

Sangster (1998). The ends of needle segments were planed to a smooth, flat surface using a diamond knife in a cryomicrotome at -80°C . Needle segments were then carbon-coated prior to energy-dispersive X-ray (EDX) microanalysis on the cold stage of a JEOL 6,400 cryo-scanning electron microscope (cryo-SEM) at -170°C . In order to evaluate mineral contents, analyses were conducted in the following six leaf tissues: the epidermis outer tangential wall (OTW); the hypodermis inner tangential wall (ITW); the mesophyll radial wall; the endodermis OTW; the transfusion radial walls (the transfusion is the layer immediately surrounding the vascular bundles) and lastly, the walls of the xylem.

Quantitative data were obtained for aluminium (Al) and silicon (Si) with windows of 0.16 keV centred around the peaks. Beryllium and ultrathin windows were used to collect counts for a live time of 100 s using a Link eXL, LZ-4 detector (Oxford Instruments). The electron beam was focused on the cell walls at a magnification of $\times 2,000$. A raster size equivalent to a scan area at specimen level of 25 mm^2

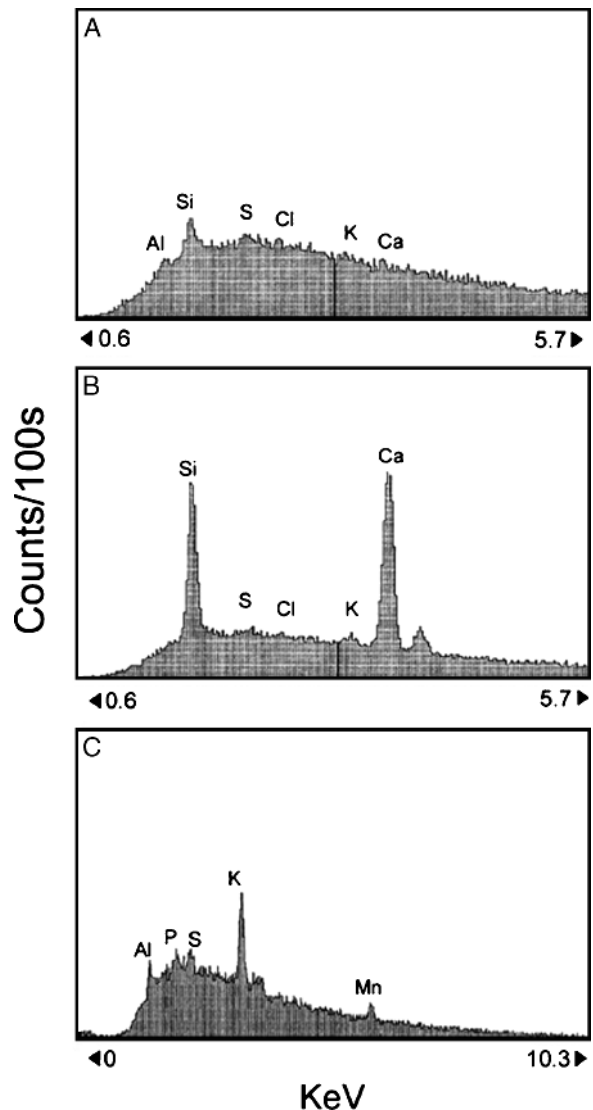


Fig. 4 Representative EDX microanalysis spectra from Douglas fir needle tissues, from the Can. site (**A** and **B**) and the Fr. site (**C**). Full vertical scales (VS) in counts are variable according to the area analyzed. Horizontal spectral ranges are in KeV. Transverse sections; about 2 mm from the tip of the frozen hydrated needles. **A**, epidermis OTW, 2 year needle; VS=1,600. **B**, hypodermis OTW, 2 year needle; VS=3,200. **C**, transfusion cell, radial wall, 0 year needle; VS=800

was employed at an accelerating voltage of 15 kV. Counts were periodically equilibrated with a cobalt standard spectrum. At least five replicate analyses of each tissue area were performed. Data were transformed to corrected weight percentages using a ZAF-PB programme and expressed in mmol kg^{-1} .

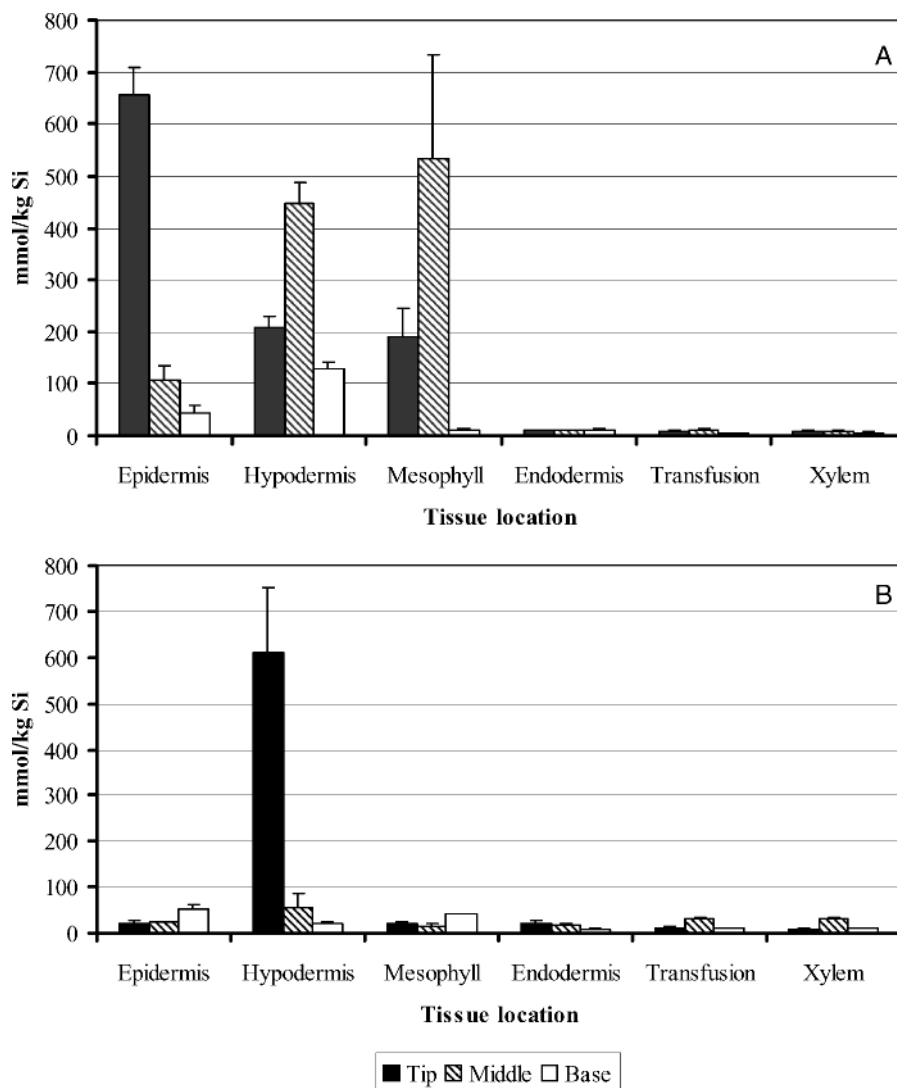
4 Results

Douglas fir leaves are linear and acuminate, from 18 to 30 mm long, growing out from three sides of the twigs (Hosie, 1979). The internal structure, shown in Fig. 1, reveals the thickened paradermal walls of the epidermis and hypodermis. The mesophyll of this

species has both palisade parenchyma and spongy mesophyll, unusual for a conifer (Mauseth, 1988). However, in the closely packed tissues at the leaf tip shown in Fig. 1, only the palisade tissue is evident. The prominent endodermis surrounds the single vein consisting of peripheral transfusion tissue (a layer of tracheids and parenchyma) around the central vascular bundle. The latter, shown in Fig. 2, displays a cambium, which produces secondary phloem but no secondary xylem.

Figure 3A shows a representative secondary electron image of a transverse section at the tip of a year 2 needle (Can. site). The corresponding calcium (Ca) X-ray distribution image (Fig. 3B) shows that Ca was localized most heavily in the hypodermis OTW and

Fig. 5 Silicon distribution in the Douglas fir needle as determined by X-ray micro-analysis. Two year needles were taken from trees growing in Breuil Forest, Morvan, France (A), and from Glendon Campus, Toronto, Canada (B). Analyses were conducted in six tissue areas (epidermis, hypodermis, mesophyll, endodermis, transfusion layer and xylem wall), at the base middle and tip regions of the needles. All determinations were the means of five replicates ($\pm$ standard error), and concentrations are expressed in mmol kg^{-1}



also in the epidermal wall. These two layers encircle the needle except for the lower surface. The matching Si X-ray distribution image (Fig. 3C) displays preferential loading of Si in the epidermal and hypodermal OTW, and in the transfusion tissue, with lesser amounts in the mesophyll. The two dermal Si layers encircle the leaf.

Three representative spectra from tissue analyses of the tip region of frozen hydrated needles are presented in Fig. 4. These are from individual spot analyses with the beam focused on specific tissue walls. Figure 4A displays the spectrum produced by the OTW of the epidermis of a year 2 needle (Can. site). The major mineral peaks were those for Si, Al, Ca, sulphur (S), chlorine (Cl), and potassium (K). In contrast, the spectrum in Fig. 4B for the walls of the immediately adjacent hypodermis indicated high concentrations of both Si and Ca. In Fig. 4C, an example from the vascular bundle of a needle from the Fr. site, the transfusion cell wall registered peaks for Al, phosphorus (P), S and K. There was also a distinct peak for manganese (Mn).

Quantitative estimates of Si distribution in year 2 needles are presented in Fig. 5. It is clear that Si levels were relatively low in the internal tissues (endodermis, transfusion layer and xylem wall), in both Fr. and Can. needles. In the needles from the Can. site only the hypodermis at the tip was high in Si, whilst Si deposition was generally much greater in the needles from the Fr. site in the epidermis, hypodermis and mesophyll.

Aluminium analysis revealed that there were few major areas of concentration in needles from either of the sites (Fig. 4A and C were exceptions). Although the Fr. site had a mean Al concentration (taken over all tissues and all needle positions) of $10.4 \text{ mmol kg}^{-1}$ against 9.1 for the Can. site ($n=90$) this difference was not significant at the 0.05 level.

5 Discussion

Of the elements detected in this investigation, four (K, P, S and Cl) were more or less ubiquitous in the needle tissues at both sites (Fig. 4). Manganese peaks, as in Fig. 4C, infrequently were encountered in needle tissues, and only from the Fr. site. This heavy metal, frequently associated with acidic soils, has been

detected in needles of other conifers from acidic sites by Hodson and Sangster (1998, 2002). Calcium deposition reached highest levels in Douglas fir needles in the epidermis and hypodermis (Figs. 2b and 4B), whilst in white spruce the epidermis and mesophyll had the highest concentrations (Hodson & Sangster, 1998), and in white pine, the epidermis, transfusion and endodermis were major sites of deposition (Hodson & Sangster, 2002).

5.1 Silicon

Silicon is unevenly distributed in the Douglas fir needle (Figs. 3C and 5). The highest Si content occurs in the epidermal and hypodermal layers and internally in the mesophyll. The two outer Si layers completely encircle the needle (Fig. 3c). The x-ray distribution image also indicates the pathway that soluble Si might follow. Silicic acid in the transpiration stream, which accumulates in the transfusion tracheids (clusters of bright dots at the centre of Fig. 3c), would move outwards symplastically through the endodermis, and thence across the mesophyll to reach the outer layers. Canny (1993) discussed this flow pathway in considerable detail for the pine needle, in the course of which, a hypothesis predicting solute build-up in the conifer needle tip was advanced. As water transpires, the silicic acid dissolved in it becomes supersaturated and eventually polymerizes forming silica gel, which becomes incorporated in the cell wall termini of the transpirational water flux (Fig. 1).

Tissues of needles of Douglas fir from the Fr. site exhibited the highest Si content, which increased from needle base to tip (Fig. 5). Comparisons with the results for Si distribution in other conifer leaves, including spruce, larch and pine, reveal differences as to the tissues receiving the heaviest Si loading. However, the epidermis, hypodermis and mesophyll were commonly utilized. In Douglas fir from the Can. site Si deposition is almost entirely confined to the hypodermis at the tip of the needle (Fig. 5). The hypodermis has previously been shown to be a major site of Si accumulation in white spruce (Hodson & Sangster, 1998). Usually, it has been observed that the heaviest deposition occurs in needle tips, except in the case of spruce. A more detailed comparison has been made elsewhere (Hodson & Sangster, 2002). In studies of spruce, pine (Hodson & Sangster, 1998,

2000, 2002) and now Douglas fir, Si content was always greater in needles from acidic sites. Perhaps this occurs because the weathering of acidic soils under coniferous forests releases more Si. Bartoli (1983) determined that whereas $29.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ of Si was released under a coniferous forest ecosystem in eastern France, by comparison, only $2.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ were released under a deciduous forest ecosystem. Apart from soil factors, genotypic or ecotypic variation among tree cultivars may be invoked to account for differences in biomineralization of tissues.

5.2 Aluminium

One of the, perhaps unexpected, findings of this investigation was that there was no significant difference in Al concentration between the needles taken from soil with pH 6.7 (Can.) and soil with 4 to 4.5 (Fr.). As Al availability is increased at low soil pH, it might be expected that needle Al concentration would be higher in plants growing in a more acidic soil. However, previous chemical analyses (Beaton et al., 1965; Stefan, Fürst, Hacker, & Bartels, 1997) of Douglas fir needles from trees growing in a variety of environments, and with variable soil pH, have shown that Al concentrations do not vary greatly between sites. Chemical analyses of needles from the Fr. site for Al content (Prabagar, unpublished) fitted well within the previously determined range. The explanation for the lack of variation in needle Al concentration in Douglas fir with soil pH is obscure, but may be related to sequestration of Al in the roots of this species and/or to the presence of an exclusion mechanism for Al.

5.3 Comparison of X-ray Microanalysis with Bulk Mineral Analysis

It is fairly rare that X-ray microanalysis has been performed on plant material similar to that subjected to chemical analysis, and it is interesting to compare the present results for the Fr. site with unpublished chemical analyses from our laboratory (Prabagar et al. unpublished). To compute the elemental concentrations the ZAF-PB programme we used assumed a matrix of cellulose, and the microanalysis results were expressed in mmol kg^{-1} . Needles from the Fr. site had

a mean Al concentration of $10.4 \text{ mmol kg}^{-1}$ using microanalysis, and about $14 \text{ } \mu\text{mol g d.wt.}^{-1}$ using chemical analysis. The difference between the two values could easily be accounted for by water in the samples analysed using microanalysis. The comparison with Si is more complex, as the element is not evenly distributed within the tissues of the needle (Fig. 5). Concentrations determined using microanalysis vary from 655 mmol kg^{-1} Si in the epidermis at the tip of the needle to only 6.6 mmol kg^{-1} in the transfusion tissue at the base. Chemical analysis of year 1 needles showed that they contained $363.8 \text{ } \mu\text{mol g d.wt.}^{-1}$ Si. Clearly, chemical analysis of a Douglas fir needle for Si is a composite mean of the concentrations in the various needle tissues. There are many complexities in the types of comparisons we have undertaken here, but it is nevertheless a valuable exercise, if only to confirm the accuracy of the analyses.

5.4 Al/Si Interactions

In the last few years, many workers have observed the phenomenon of Al/Si codeposition in plant tissues, and most particularly in the conifers (Hodson & Sangster, 1999). Such codeposition was first reported in Norway spruce (Godde, Homburg, Methfessel, & Rosenkranz, 1988), but has since been noted in eastern white pine (Hodson & Sangster, 1999, 2000, 2002), white spruce (Hodson & Sangster, 1998), eastern (American) larch and European larch (Sangster et al., 2001), and balsam fir (Sangster & Hodson, 2001). In some species Al/Si codeposits are most frequently located in the epidermis (white spruce and the larch species), but in others the transfusion tissue is a major location (white pine, Norway spruce). Godde et al. (1988) suggested that Al/Si codeposition was only common in Norway spruce plants that are suffering Al stress, and undoubtedly the amount of available Al in the soil affects the amount of codeposition. In the present investigation, Al/Si codeposition was only rarely encountered in Douglas fir (Fig. 4A) and this appears consistent with the absence of toxicity signs in the Douglas fir forest planted at the Breuil field site. Douglas fir needles from the Fr. site had a mean Al concentration of $10.4 \text{ mmol kg}^{-1}$ over all tissues, and a maximum value of 28 mmol kg^{-1} . For comparison the transfu-

sion cells of white pine analysed from the Can. site (soil pH 6.7), from Muskoka (soil pH 4.2) and from Sudbury (soil pH 3.5 to 4.0) contained mean concentrations of 9.1, 44.5 and 61.4 mmol kg⁻¹ Al, respectively (Hodson & Sangster, 2000). Evidently Al levels detected in Douglas fir needles, even from the Fr. site, were considerably below those in white pine from acidic soils. It seems that Al is fairly evenly spread through the needles of Douglas fir trees from both of the collection sites, and that pronounced codeposition may only be observed in trees that are under more severe Al stress.

Acknowledgements The authors wish to thank J. Ranger (INRA, Nancy), field site scientific manager, and D. Gelhaye, technical manager of the Breuil Forest site, for their assistance with this work. Microanalytical data were obtained at the Research Facility for Electron Microscopy, Carleton University, Ottawa, Canada. Financial support was received from York University (A.G.S.).

References

- Augusto, L., & Ranger, J. (2001). Impact of tree species on soil solutions in acidic conditions. *Annals of Forest Science*, 58, 47–58.
- Bartoli, F. (1983). The biogeochemical cycle of silicon in two temperate forest ecosystems. In R. Hallberg (Ed.), *Environmental Biogeochemistry. Ecological Bulletin (Stockholm)*, 35, 469–476.
- Beaton, J. D., Brown, G., Speer, R. C., Masrae, I., McGhee, W. P. T., Moss, A., et al. (1965). Concentration of micro-nutrients in foliage of three coniferous tree species in British Columbia. *Soil Science Society of America Proceedings*, 29, 299–302.
- Canny, M. J. (1993). Transfusion tissue of pine needles as a site of retrieval of solutes from the transpiration stream. *New Phytologist*, 123, 227–232.
- Crawford, R. H., Floyd, M., & Li, C. Y. (2000). Degradation of serpentine and muscovite rock minerals and immobilization of cations by soil *Penicillium* spp. *Phyton-Annales Rei Botanicae*, 40, 313–321.
- Curt, T., Lucot, E., & Bouchard, M. (2001). Douglas fir root biomass and rooting profile in relation to soils in a mid-elevation area (Beaujolais Mounts, France). *Plant and Soil*, 233, 109–125.
- Farrar, J. L. (2004). *Trees in Canada*, (5th edn., 502 pp). Fitzhenry and Whiteside, Toronto and Canadian Forest Service, Ottawa.
- Gérard, F., Tinsley, M., & Mayer, K. U. (2004). Preferential flow revealed by hydrologic modeling based on predicted hydraulic properties. *Soil Science Society of America Journal*, 68, 1526–1538.
- Godde, D., Homburg, H., Methfessel, S., Rosenkranz, J. (1988). Die Röntgenanalyse hilft bei der Aufklärung individueller Waldschäden. *LÖLF-Mitteilungen*, 4, 23–27.
- Hodson, M. J., & Sangster, A. G. (1998). Mineral deposition in the needles of white spruce [*Picea glauca* (Moench.) Voss]. *Annals of Botany*, 82, 375–385.
- Hodson, M. J., & Sangster, A. G. (1999). Aluminium/silicon interactions in conifers. *Journal of Inorganic Biochemistry*, 76, 89–98.
- Hodson, M. J., & Sangster, A. G. (2000). Aluminium localization in conifers growing on highly acidic soils in Ontario, Canada. In *Proceedings of the international symposium on impact of potential tolerance of plants on the increased productivity under aluminium stress* (pp. 103–106). Kurashiki, Japan: Research Institute for Bio-resources, Okayama University.
- Hodson, M. J., & Sangster, A. G. (2002). X-ray microanalytical studies of mineral localization in the needles of white pine (*Pinus strobus* L.). *Annals of Botany*, 89, 367–374.
- Hosie, R. C. (1979). *Native trees of Canada* (8th edn., pp. 82–85). Toronto: Fitzhenry and Whiteside.
- Jentschke, G., Drexhage, M., Fritz, H. W., Fritz, E., Schella, B., Lee, D. H., et al. (2001). Does soil acidity reduce subsoil rooting in Norway spruce (*Picea abies*)? *Plant and Soil*, 237, 91–108.
- Mauseth, J. D. (1988). *Plant anatomy* (p. 254). Menlo Park, CA, USA: Benjamin/Cummings.
- Sangster, A. G., & Hodson, M. J. (2001). Silicon and aluminium codeposition in the cell wall phytoliths of gymnosperm leaves. In J. D. Meunier & F. Colin (Eds.), *Phytoliths-applications in earth science and human history* (pp. 343–355). Lisse, The Netherlands: A.A. Balkema.
- Sangster, A. G., Hodson, M. J., & Huang, C. X. (2001). X-ray microanalytical studies of mineral composition in cell walls of needle tissues of American Larch [*Larix laricina* (Du Roi) K. Koch] and European Larch [*L. decidua* (L.) Mill.]. In M. Labrecque (Ed.), *L'Arbre 2000 the tree, 4th international symposium on the tree, Montreal Botanic Garden* (pp. 160–167). Montreal, Canada: Isabelle Quentin.
- Stefan, K., Fürst, A., Hacker, R., & Bartels, U. (1997). *Forest foliar condition in Europe – Results of large scale foliar chemistry surveys (survey 1995 and data from previous years)*. EC, UN/ECE, Austrian Federal Forest Research Centre.

Effects of Acid Rain on Competitive Releases of Cd, Cu, and Zn from Two Natural Soils and Two Contaminated Soils in Hunan, China

Bohan Liao · Zhaohui Guo · Qingru Zeng ·
Anne Probst · Jean-Luc Probst

Received: 15 May 2006 / Accepted: 25 October 2006 / Published online: 27 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Leaching experiments of rebuilt soil columns with two simulated acid rain solutions (pH 4.6–3.8) were conducted for two natural soils and two artificial contaminated soils from Hunan, south-central China, to study effects of acid rain on competitive releases of soil Cd, Cu, and Zn. Distilled water was used in comparison. The results showed that the total releases were $\text{Zn} > \text{Cu} > \text{Cd}$ for the natural soils and $\text{Cd} > \text{Zn} \gg \text{Cu}$ for the contaminated soils, which reflected sensitivity of these metals to acid rain. Leached with different acid rain, about 26–76% of external Cd and 11–68% external Zn were released,

but more than 99% of external Cu was adsorbed by the soils, and therefore Cu had a different sorption and desorption pattern from Cd and Zn. Metal releases were obviously correlated with releases of TOC in the leachates, which could be described as an exponential equation. Compared with the natural soils, acid rain not only led to changes in total metal contents, but also in metal fraction distributions in the contaminated soils. More acidified soils had a lower sorption capacity to metals, mostly related to soil properties such as pH, organic matter, soil particles, adsorbed SO_4^{2-} , exchangeable Al^{3+} and H^+ , and contents of Fe_2O_3 and Al_2O_3 .

B. Liao
International College, Central South University
of Forestry and Technology,
Changsha, China 410004

Z. Guo
Department of Environmental Engineering
Central South University,
Changsha, China 410083

Q. Zeng
College of Resources and Environment,
Hunan Agricultural University,
Changsha, China 410128

A. Probst (✉) · J.-L. Probst
ECOLAB, CNRS-INPT-Université Paul Sabatier,
UMR 5245, CNRS/UPS/INPT/ENSAT,
Avenue de l'Agrobiopole, BP 32607, Auzeville Tolosane,
31326 Castanet Tolosan, Cedex, France
e-mail: anne.probst@ensat.fr

Keywords acid rain · soil · leaching experiment ·
sequential extraction · Cu · Cd · Zn · China

1 Introduction

There is a growing public concern over the potential accumulation of heavy metals in agricultural soils in China owing to rapid urban and industrial development and increasing reliance on agrochemicals in the last several decades (Wong, Li, Zhang, Qi, & Min, 2002). Because of acidification processes triggered by acid rain, heavy metals are transported by the leachate via the groundwater to surface streams (Liciskó & Szebényi, 1999). Although cation exchange, surface adsorption, chelation with organic material, and

precipitation are important mechanisms for heavy metal mobility, acid rain water removes heavy metals which are weakly adsorbed in soils (Gong & Donahoe, 1997). Various soils show a very different behavior in sorption of heavy metals (Alumaa, Kirso, Petersell, & Steinnes, 2002), because the concentration of each heavy metal is always controlled by different parameters (soil pH, iron and aluminum oxide content, clay content, organic matter and cation exchange capacity) (Hernandez, L. Probst, A. Probst, & Ulrich, 2003). Various metals also exhibit different preferential leaching from soils. For example, the depletion sequence is $\text{Cd} > \text{Ni} > \text{Zn} > \text{Cu}$ in some acid soils (Wilcke & Kaupenjohann, 1998). Although Cd abundance in lithosphere is quite low, it is a typical toxic element in soil to plants (Wang, 2000). Cu and Zn are necessary trace nutrient elements to plants and human being, but high contents of Cu or Zn in soil could result in accumulation in plants and subsequently inhibit growth of plants (Fan, 1991).

Hunan, a province in south-central China, is located in the center area of acid deposition (F. Wu, J. Wu, & Wang, 2000). Meanwhile, mining activities in Hunan have been conducted for more than 500 years, which has resulted in heavy metal contamination in soils, rivers, and crops in the mining areas, and even some environmental accidents (Liu, Probst, & Liao, 2005). However, there are few published reports on chemical behaviors of soil heavy metals influenced by acid rain in this area. We wonder how trace metals in the natural soils respond to acid rain, and what will happen if the soils are contaminated with heavy metals and exposed to serious acid rain. In this study, we conducted leaching experiments with two simulated acid rain solutions for two natural soils from Hunan and two artificial contaminated soils. The primary objectives of this study were to investigate effects of acid rain on competitive releases of Cd, Cu, and Zn from natural soils and from contaminated soils, and to compare changes in fractions of these metals in soil profile affected by

acid rain, because Cd, Cu, and Zn are main contaminating metals in Hunan mining areas and their ambience.

2 Materials and Methods

Two natural soil profiles were selected from the mountainsides, one from the suburb of Changsha ($28^{\circ}23'\text{N}$, $113^{\circ}17'\text{E}$) in northern Hunan and the other from Chenzhou ($25^{\circ}48'\text{N}$, $113^{\circ}02'\text{E}$) in southern Hunan. The soil from Changsha is red soil, marked as Soil A, and the main vegetation is China fir (*Cunninghemia lanceolata*). The soil from Chenzhou is yellow red soil, marked as Soil B, covering with mixed China fir (*Cunninghemia lanceolata*), Masson pine (*Pinus massoniana*), and bushes, and mining activities in Hunan mostly happen in this area. These two soils, both developed from Quaternary red clay (belonging to Allitic Udic Ferrisols in FAO system), are very typical soils in southern China. For each profile, the soil samples from three layers (20 cm for each layer, marked as topsoil, subsoil, and bottom soil, respectively) were collected, aired dried, and passed through a 2 mm sieve for further experiments.

Soil columns were rebuilt in washed PVC tubes (65 cm for the height and 7.1 cm for the diameter) according to the natural profiles. First, 1.1 kg of bottom soil was put into the column, and then followed by 1.0 kg of subsoil and 1.0 kg of topsoil. The height of each layer was about 20 cm, separating with a thin layer of sponge. According to the compositions of precipitation during the period of 1990–1998 in Chenzhou and Changsha (Wu et al., 2000), we prepared two simulated acid rain solutions for the leaching experiments, marked as AR2 and AR3, respectively, and distilled water (marked as AR1) was used in comparison. The pH and main compositions were given in Table 1. From AR1 to AR3, the pH values were decreased and total dissolved salts increased.

Table 1 pH values and major ion concentrations of simulated acid rain ($\mu\text{mol l}^{-1}$)

Code	pH	Ca^{2+}	NH_4^+	Mg^{2+}	K^+	Na^+	SO_4^{2-}	NO_3^-	Cl^-
AR1	5.74	0	0	0	0	0	0	0	0
AR2	4.56	52.40	57.50	4.94	7.29	13.70	80.65	20.81	21.06
AR3	3.78	69.86	76.67	6.58	9.72	18.26	107.50	27.74	156.39

Two sets of leaching experiments were conducted, one for the natural soils and the other for the contaminated soils. In order to simulate contamination processes in the field, and to compare releases of the different metals from soils influenced by acid deposition on the same basis, the contaminated soils were prepared by adding 100 ml solution containing 200 mg of each metal Cd, Cu, and Zn (in the form of pure CdCl_2 , CuCl_2 , and ZnCl_2 , respectively) evenly to the top of the natural soil column, and then equilibrated for 15 days. Calculated from annual about 1,500 mm precipitation in Hunan and about 50% evapotranspiration, each soil column was leached for 60 days with a total of 29.7 l simulated acid rain solution (495 ml for each day), which corresponded to the local precipitation of about 10 years. To simulate the field situation, an intermittent leaching process was adopted and the leaching rate was controlled at $30 \pm 5 \text{ ml h}^{-1}$, i.e. about 16 h for leaching and 8 h for drying each day. The leachates were collected every 6 days and 10 leachates were obtained from each column. All leachates were filtrated through $0.45 \mu\text{m}$ membrane and stored at 4°C . Meanwhile the soil samples from every 10 cm in the columns were collected, air dried, and stored for further analysis. The triplicate leaching experiments were conducted.

Basic physicochemical properties of the two natural soils (Table 2) and some soil parameters before leaching were determined according to Chinese standard methods for soil analysis (Lu, 1999). Contents of soil organic matter were determined by a volumetric method of $\text{K}_2\text{Cr}_2\text{O}_7$ -heating, cation exchange capacity (CEC) and base saturation (BS) were determined by extracting with a $1.0 \text{ mol l}^{-1} \text{ NH}_4\text{OAc}$ solution (pH 7.0). The total contents of soil heavy metals were determined directly by acid digestion using a mixture of $\text{HF}/\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{O}_2$ on hot plates at atmospheric pressure. Following the operational procedures of Chao (1972), Tessier, Campbell, and Blason (1979), Shuman (1982) and more recently, Leleyter and Probst (1999), heavy metal speciation in the soils was studied and divided into six fractions: exchangeable including water soluble (Ex), bound to manganese oxides (OMn), bound to organic matter (OM), bound to amorphous iron oxides (AOFe), bound to crystalline iron oxides (COFe), and residue (Res). Metals in the solutions were determined on atomic absorption spectroscopy with a graphite furnace (AAS, Shimadzu AA-6800), and the detection limit for Cd, Cu, and Zn was lower than $1 \mu\text{g l}^{-1}$. Analysis uncertainties of metals on AAS were estimated by analyzing the replicated soil solutions, and the average standard deviations were about 5% for all metals.

Table 2 Basic physicochemical property of the natural soils

Parameters		Soil A (Red soil)			Soil B (Yellow red soil)		
		0–20 cm	20–40 cm	40–60 cm	0–20 cm	20–40 cm	40–60 cm
Soil sampling site		Changsha			Chenzhou		
pH value		4.72	4.97	4.83	4.48	4.53	4.57
Content of organic matter (g kg^{-1})		21.99	18.46	16.10	20.87	5.26	4.54
Cation exchange capacity (CEC, cmol kg^{-1})		10.06	10.32	10.09	11.63	9.46	9.41
Bases saturation (BS, %)		14.40	11.75	12.47	12.54	10.95	12.32
Content of adsorbed sulfate (g kg^{-1})		10.97	8.19	8.32	16.32	18.25	16.40
Content of exchangeable acidity	H^+	0.27	0.22	0.21	0.25	0.21	0.18
(cmol kg^{-1})	$1/3\text{Al}^{3+}$	4.07	4.26	4.49	4.89	4.96	4.72
Content of soil particles (%)	$>0.05 \text{ mm}$	17.51	19.3	18.38	25.78	20.92	30.16
	$0.05\text{--}0.02 \text{ mm}$	6.27	7.15	8.16	6.19	8.22	6.16
	$<0.02 \text{ mm}$	76.23	73.55	73.46	68.04	70.87	63.67
Content of oxides (g kg^{-1})	Al_2O_3	2.25	2.31	2.14	1.74	2.48	2.44
	Fe_2O_3	3.44	3.44	3.63	5.78	3.83	3.55
Total content of heavy metals (mg kg^{-1})	Cd	1.23	1.07	0.71	1.87	1.40	0.74
	Cu	32.99	21.01	22.42	21.22	17.93	18.56
	Zn	243.51	276.97	275.87	289.40	300.82	289.01

3 Results

3.1 Competitive Releases of Soil Heavy Metals Affected by Acid Rain

When the pH values decreased from 5.7 to 3.8 in simulated acid rain solutions, the accumulative releases

of heavy metals (the sum of metal contents in the 10 leachates) increased significantly (Fig. 1). For the natural soils, the release trends of Cd, Cu, and Zn were almost linearly increased with increasing in leaching volumes ($R^2 > 0.990$; $n = 10$, $\rho_{0.01} = 0.585$). The final releases for these three metals were Zn (1.2–2.2 mg) > Cu (0.86–1.5 mg) > Cd (0.26–0.38 mg),

Fig. 1 Effects of acid rain on accumulative releases of Cd (*above*), Cu (*middle*), and Zn (*below*) from the natural soils and the contaminated soils. “N” was the natural soils and “C” the contaminated soils. AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing). The accumulative release presented the sums of metal contents in the leachates and 10 leachates were collected during the leaching process

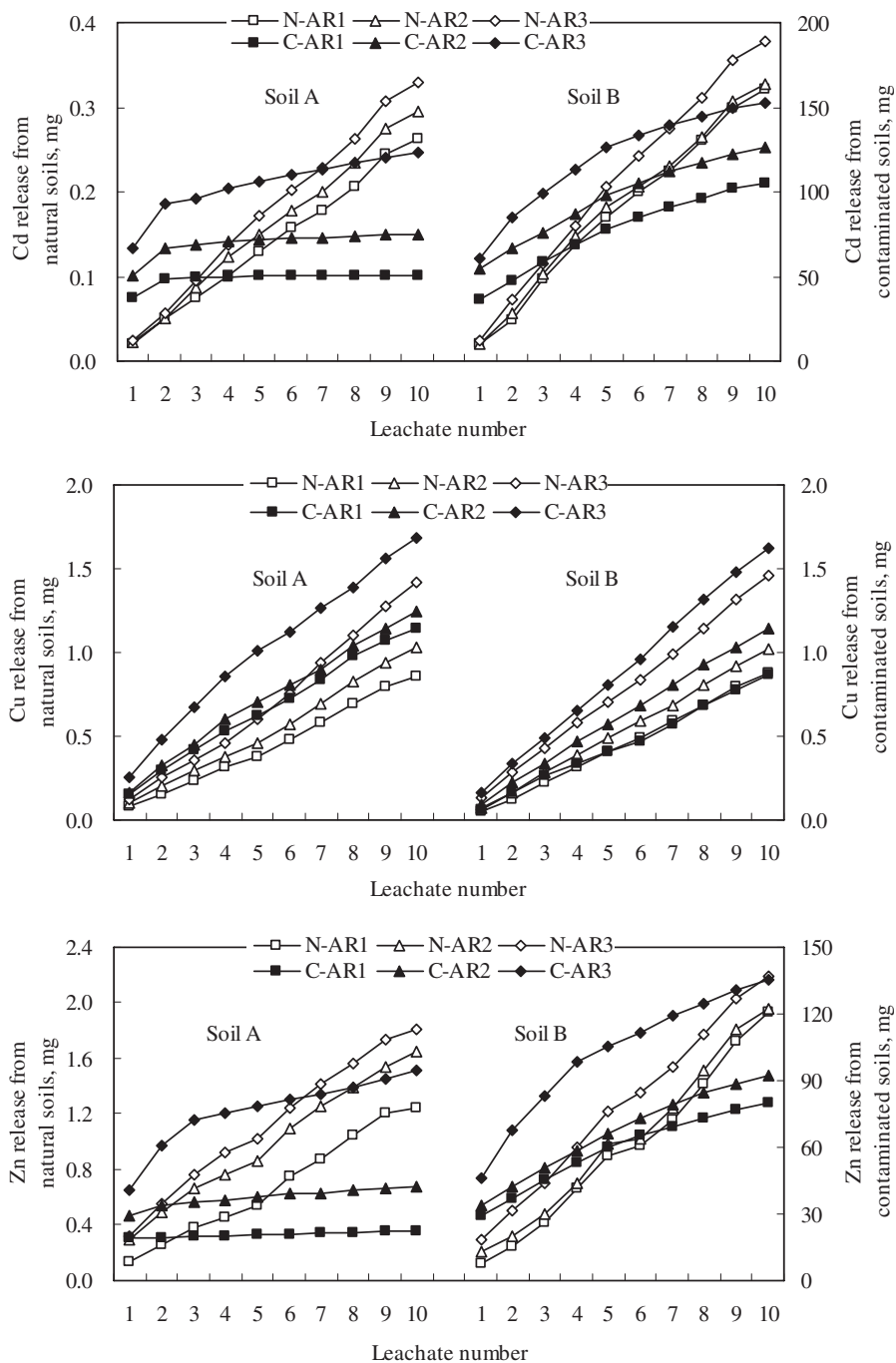
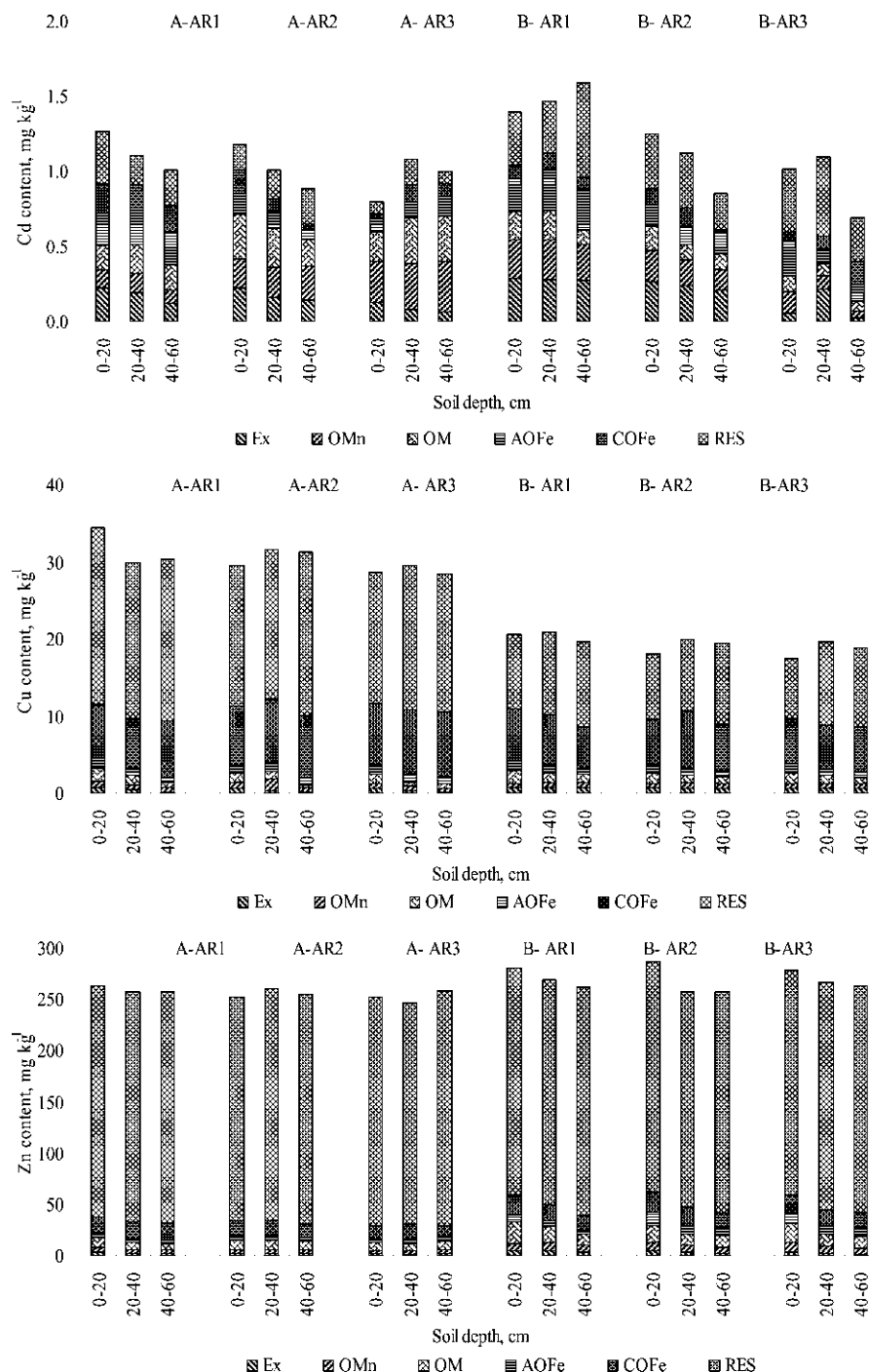


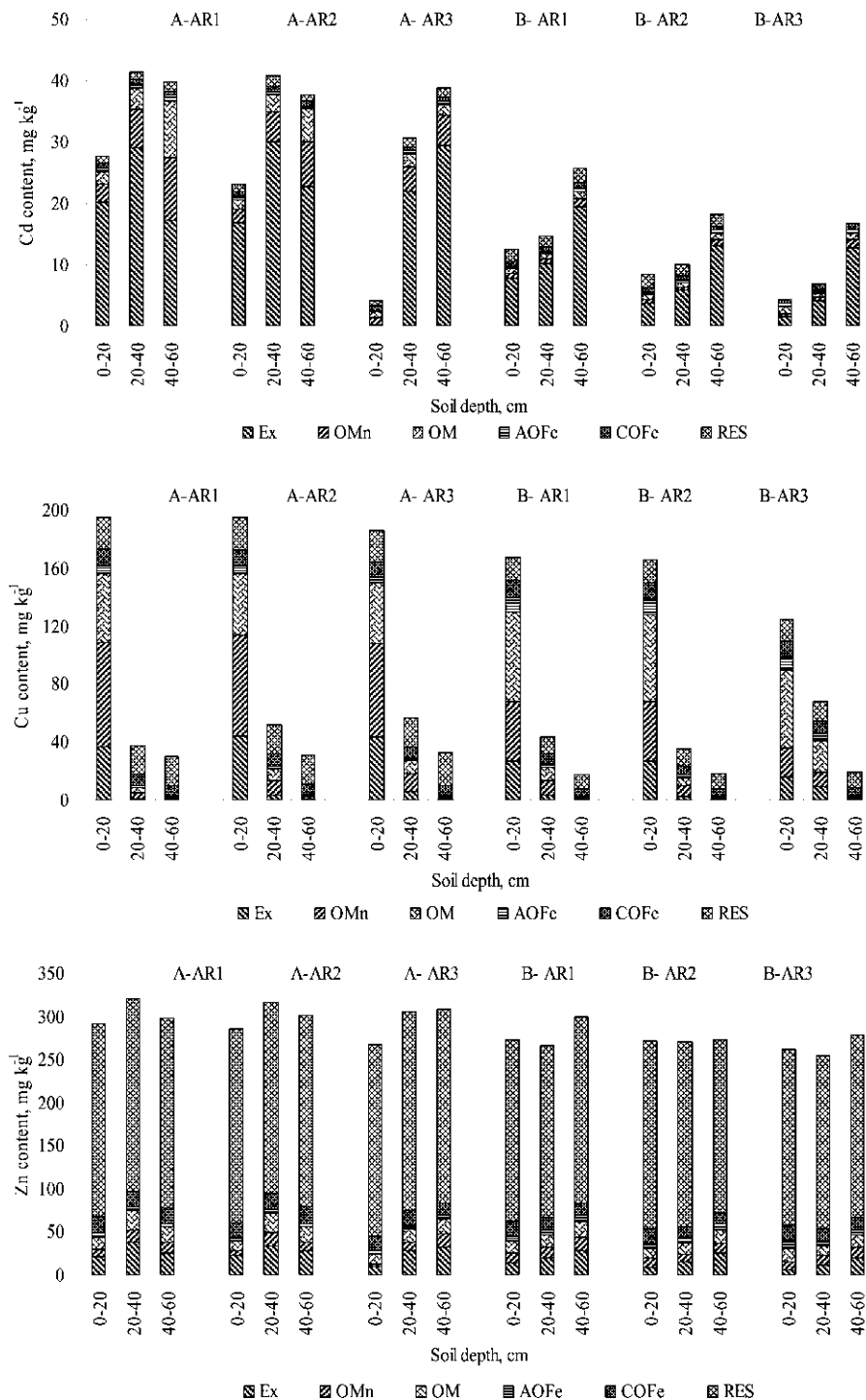
Fig. 2 Effects of simulated acid rain on fraction contents of Cd (*above*), Cu (*middle*), and Zn (*below*) in the natural soils. A meant Soil A (*left*), B meant Soil B (*right*). AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing). Ex: exchangeable; OMn: bound to manganese oxides; OM: bound to organic matter; AOfFe: bound to amorphous iron oxides; COFe: bound to crystalline iron oxides; Res: residue



and this sequence corresponded to soil metal contents. Compared with Soil A, the releases of Cd and Zn were higher from Soil B due to higher soil total contents of Cd and Zn; however, Cu releases were almost the same in the two soils, although Soil A had higher Cu content

than Soil B (Table 2). For the contaminated soils, the accumulative releases were greatly enhanced for Cd (51–153 mg) and Zn (22–136 mg) owing to external addition, but not for Cu. Cu releases from the contaminated soils (0.87–1.69 mg) were almost the

Fig. 3 Effects of simulated acid rain on fraction contents of Cd (*above*), Cu (*middle*), and Zn (*below*) in the contaminated soils treated with 200 mg of each element. A meant Soil A (*left*), B meant Soil B (*right*). AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing). Ex: exchangeable; OMn: bound to manganese oxides; OM: bound to organic matter; AOFc: bound to amorphous iron oxides; COFe: bound to crystalline iron oxides; Res: residue



same as those from the natural soils, and there were no obvious differences between the two soils. This meant that the sorption capacity of these two soils to Cu was great. The release sequence in the contaminated soils

was $Cd > Zn > Cu$, showing that external Cd in soils was the most sensitive to acid rain, followed by Zn. Most external Cu was adsorbed by soils and did not show sensitivity to acid rain.

3.2 Effects of Acid Rain on Metal Distribution in the Natural Soils

The fraction distribution of Cd, Cu, and Zn in the natural soils affected by simulated acid rain was given in Fig. 2. For Cd, six fractions were basically evenly distributed in the both soils. Ex forms were decreased from the topsoil to the bottom soil in Soil A and from AR1 to AR3, but no special pattern was observed for the other fractions. For Cu, the most important fractions were Res and COFe forms. Affected by acid rain (AR2 and AR3), Res forms in the topsoil were lower than those in the subsoil or bottom soil, probably due to mineral dissolution at lower pH. But for the Ex, OM, and AOFe forms of Cu, the contents were generally declined from the topsoil to the bottom soil. For Zn, Res form was the dominant fraction. Because the final releases accounted for only 0.15–0.24% compared with the total contents in the soils, there were no significant changes for Zn among the different treatments of simulated acid rain solutions. After leaching, the total contents of Cd and Zn were higher in Soil B than in Soil A, and those of Cu had a reverse result of Cd and Zn.

3.3 Effects of Acid Rain on Metal Distribution in the Contaminated Soils

Compared with the natural soils, the contaminated soils had different fraction distributions, especially for Cd and Cu (Fig. 3). The most important Cd fraction was Ex form, followed by OMn and OM forms in Soil A and Res form in Soil B. Because of leaching process, the total contents and Ex fraction increased generally from the topsoil to the subsoil or bottom soil, indicating a higher migration of Cd in soil profiles accompanied with leachates. From AR1 to AR3, the total Cd contents were obviously decreased, particularly in the topsoil, showing a higher sensitivity of external Cd to acid rain. Most Cu content was found in the topsoil where it was regularly distributed among the different fractions. Only a small part of external Cu was transferred to the lower soil layers, showing a greater sorption capacity to Cu for these two soils, so that a clear sequence of Cu contents was obtained as topsoil > subsoil > bottom soil. The Cu contents of Ex, OMn, and OM forms enhanced quite a lot because of addition of external Cu. With

increasing in acidity and total dissolved salts in acid rain, the total Cu content decreased in the topsoil and increased in the subsoil or bottom soil. In the two contaminated soils, residue Zn (Res) was still the dominant fraction, but the other fractions increased to different degrees. Exchangeable Zn (Ex) was the second important form, and increased from the topsoil to the bottom soil in most cases, especially in Soil B, demonstrated that Ex Zn, mostly coming from the external source, was sensitive to acid rain and easily transferred through soil columns. Compared with Soil B, the total contents of Cd, Cu, and Zn were all higher in Soil A, further implying a greater sorption capacity to heavy metals for Soil A.

3.4 Comparison between Metal Releases and Contents in Soils

Under the affection of simulated acid rain, the final releases of Cd, Cu, and Zn from the natural soils were all increased from AR1 to AR3 (Fig. 1), and accounted for 7.8–10.7%, 1.1–2.5%, and 0.15–0.24% in the total contents of Cd, Cu, and Zn, respectively (Table 3). It was clear that increasing acidity in acid rain resulted in increasing metal releases from the natural soils. In the contaminated soils, the total contents enhanced 200 mg for each element due to addition of external sourced heavy metals. In these cases, the final releases of Cd and Zn were greatly increased with treatments of acid rain, and accounted for 25–75% and 2.2–12.2% of the total Cd and Zn, respectively. Because most of soil Cd came from the external source (around 98%), these percentages for Cd were almost the same as for the external Cd. However, due to only a small part soil Zn coming from the external source (around 19%), the percentages increased to 11–47% for Soil A and 40–68% for Soil B when compared with the external added Zn. From this point, the releases of Cd and Zn from the contaminated soils due to affection of acid rain were mostly from the external source. Although a large part soil Cu came from the external source (72–77%), the final releases of Cu from the contaminated soils were only slightly higher than those from the natural soils (Fig. 1), accounting for 0.3–0.6% of the total Cu or 0.4–0.8% of the external sourced Cu. These percentages were much lower than those for Cd and Zn. A comparison between final metal releases

Table 3 Comparison between the final metal releases from the natural and contaminated soils affected by acid rain and the metal total content in the corresponding soils, and ratios of the final releases from the contaminated soils to those from the natural soils

Items	Soil A			Soil B		
	Cd	Cu	Zn	Cd	Cu	Zn
<i>For the natural soils</i>						
Release (AR1)/Total content, %	8.53	1.09	0.15	7.84	1.47	0.21
Release (AR2)/Total content, %	9.58	1.31	0.20	8.04	1.71	0.22
Release (AR3)/Total content, %	10.69	1.80	0.22	9.24	2.46	0.24
<i>For the contaminated soils</i>						
Release (AR1)/Total content, %	25.1	0.40	2.20	51.6	0.30	7.20
Release (AR2)/Total content, %	37.0	0.40	4.10	61.8	0.40	8.30
Release (AR3)/Total content, %	60.7	0.60	9.20	74.8	0.60	12.2
Release (AR1)/External addition, %	25.5	0.60	11.1	52.6	0.40	40.0
Release (AR2)/External addition, %	37.5	0.60	21.2	63.1	0.60	46.2
Release (AR3)/External addition, %	61.6	0.80	47.2	76.3	0.80	67.8
<i>Ratios of the releases of the contaminated soils to those of the natural soils</i>						
AR1	193.9	1.3	17.9	328.6	1.0	41.4
AR2	254.4	1.2	25.7	384.4	1.1	47.1
AR3	374.1	1.2	52.3	404.5	1.1	61.8

from the contaminated soils and from the natural soils showed that 194–405, 18–62, and 1.0–1.3 times higher releases could be resulted in for Cd, Zn, and Cu, respectively, by the treatments of simulated acid rain solutions. This implied that for the external sourced heavy metals, the sorption capacity of the two tested soils was $\text{Cu} \gg \text{Zn} > \text{Cd}$. In other words, acid rain would remove most external Cd out from the soils, but has no special effects on movement of soil Cu and most external Cu (<99%) would be retained inside the soils.

4 Discussion

A regression analysis indicated that the accumulative releases of heavy metals (ARHM) in the 10 leachates from the contaminated soils were significantly exponentially proportional to the accumulative releases of total organic carbon (ARTOC) in the leachates: $\text{ARHM (mg)} = a \times [\text{ARTOC (mg)}]^b$, where a and b were constants (Table 4). This showed that the release of soil metals was controlled by the contents of total organic carbon to a great extent, and was similar to the results of Strobel, Hansen, Borggaard, Andersen, and Raulund-Rasmussen (2001) and Tipping et al. (2003). Special low values of coefficient a for Cu indicated that Cu was highly associated with soil

organic matter and not released into soil solution. The correlation coefficients were much higher than the level of $\rho_{0.01}$ ($n=10$, $\rho_{0.01}=0.585$) for all three elements and for all three acid rain treatments, resulting in possibility in some cases to evaluate heavy metal releases from measuring TOC contents in soil solutions.

Exchangeable fractions and total amounts of heavy metals in the contaminated soils after leaching were correlated with contents of Fe_2O_3 , Al_2O_3 , adsorbed SO_4^{2-} , exchangeable Al^{3+} or H^+ in the soils (Table 5). These relationships clearly exhibited the similar chemical behaviors for soil Cd and Zn, but quite different from Cu. Exchangeable Cd or Zn and total Cd or Zn were significantly negatively proportional to total contents of Fe_2O_3 , adsorbed SO_4^{2-} , and exchangeable Al^{3+} , and significant positive relationships between total amounts of soil Cd or Zn and total contents of Al_2O_3 were also obtained, which was similar to the results of Hernandez et al. (2003). Exchangeable Al^{3+} might markedly reduce metal sorption, for instance Cd and Zn, due to its strong affinity for the sorption sites (Phillips, 1999) and strong competition with other metals. Contrast to Cd and Zn, exchangeable Cu and total Cu had only significantly positive linear relationships with exchangeable H^+ among various characteristics in the soils. Meanwhile, exchangeable Cu and total Cu were

Table 4 Relationships between the accumulative releases of heavy metals and total organic carbon in the leachates from the contaminated soils treated with different simulated acid rain

$$\text{ARHM (mg)} = a \times [\text{ARTOC (mg)}]^b$$

Simulated acid rain	Heavy metals	Soil A			Soil B		
		a	b	R^2 ($n=10$)	a	b	R^2 ($n=10$)
AR1	Cd	28.1	0.126	0.722**	5.47	0.645	0.994**
	Cu	7.10×10^{-3}	1.02	0.997**	8.73×10^{-4}	1.50	0.988**
	Zn	14.1	0.088	0.916**	4.55	0.625	0.992**
AR2	Cd	27.9	0.210	0.803**	13.1	0.502	0.969**
	Cu	2.89×10^{-3}	1.25	0.995**	2.13×10^{-3}	1.40	0.991**
	Zn	14.4	0.220	0.973**	6.31	0.592	0.966**
AR3	Cd	18.9	0.396	0.937**	11.1	0.605	0.990**
	Cu	2.74×10^{-3}	1.35	0.989**	2.51×10^{-3}	1.47	0.990**
	Zn	6.87	0.556	0.931**	6.84	0.686	0.982**

ARHM meant the accumulative release of each heavy metal in the 10 leachates, and ARTOC the accumulative release of total organic carbon in the 10 leachates. AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing)

** meant very significant ($n=10$, $\rho_{0.01}=0.585$)

positively related to contents of Fe_2O_3 and exchangeable Al^{3+} , although not significantly, which was also different from Cd and Zn.

Soil B had a lower sorption capacity to heavy metals than Soil A. In the natural soil profiles, Soil B had lower pH values, organic matter, base saturation, and soil particles smaller than 0.02 mm, but higher contents of adsorbed SO_4^{2-} and exchangeable Al^{3+} ,

compared with Soil A (Table 2), indicated that Soil B had been more acidified. The lower sorption capacity to heavy metals for Soil B could probably be a consequence of these characteristics, because metal solubility was controlled by soil characteristics such as pH, organic matter content, soil mineralogy (Martínez & Motto, 2000). Therefore, we could speculate that plants and groundwater in Chenzhou

Table 5 Relationships between the contents of exchangeable and total heavy metals and the soil parameters in the contaminated soils treated with different simulated acid rain

Soil parameters	Relations	$n=36$, $\rho_{0.01}=0.178$					
		Ex. Cd	Total Cd	Ex. Cu	Total Cu	Ex. Zn	Total Zn
Total Fe_2O_3 , g kg^{-1}	R^2	0.491**	0.576**	0.028	0.073	0.531**	0.490**
	+/-	—	—	+	+	—	—
Total Al_2O_3 , g kg^{-1}	R^2	0.157	0.201**	0.105	0.102	0.094	0.273**
	+/-	+	+	+	+	+	+
Adsorbed SO_4^{2-} , g kg^{-1}	R^2	0.293**	0.345**	0.131	0.128	0.184**	0.408**
	+/-	—	—	—	—	—	—
Exchangeable Al^{3+} , mg kg^{-1}	R^2	0.370**	0.567**	0.016	0.021	0.325**	0.461**
	+/-	—	—	+	+	—	—
Exchangeable H^+ , mg kg^{-1}	R^2	0.066	0.074	0.532**	0.551**	0.090	0.040
	+/-	—	—	+	+	—	—

There were a total 36 contaminated soil samples, including two sets of soil columns (Soil A and Soil B, treated with three simulated acid rain solutions AR1, AR2, and AR3, and each soil column with six layers 10 cm for each layer)

+ meant the positive relations, — the negative relations, and ** very significant at the level of $\rho_{0.01}=0.178$ ($n=36$)

where Soil B collected were more fragile to suffer complex contamination of heavy metals and acid rain.

5 Conclusions

Under the effects of acid rain, the release sequences were $Zn > Cu > Cd$ in the natural soils corresponding to soil metal contents and $Cd > Zn > Cu$ in the contaminated soils, indicating that different metals had different sorption and desorption behaviors. With increasing in leaching volumes and in acidity (and total dissolved salts) of acid rain, more metals were released. In the contaminated soils, about 26–76% of external Cd and 11–67% external Zn were removed by simulated acid rain, but more than 99% of external Cu was adsorbed by the soils. The enhanced Cd in the soils was mostly exchangeable, and gradually moved down through the soil columns; however, most enhanced Cu including the fractions bound to exchangeable, manganese oxides, and organic matter was found in the topsoil. Residue Zn was still dominant in the contaminated soils after leaching, but total and exchangeable Zn increased quite a lot. Except the acidity of acid rain, the accumulated releases of heavy metals (ARHM) were closely correlated with the accumulative releases of total organic carbon (ARTOC) in the leachates, and an equation $ARHM(mg) = a \times [ARTOC(mg)]^b$ could be used to quantify metal desorption under acid rain influence. Soil sorption capacities to heavy metals were related to soil properties, such as pH, organic matter, base saturation, soil particles, adsorbed SO_4^{2-} , exchangeable H^+ and Al^{3+} , contents of Fe_2O_3 and Al_2O_3 . Generally, the soil having been more acidified had a lower sorption capacity to heavy metals, for instance Soil B from Chenzhou area in southern Hunan, China, where mining activities have being conducted. Some environmental accidents happened in 1985 in this area, and a recent field investigation showed contamination of heavy metals in the local soils and crops (Liu et al., 2005). Therefore, we could deduce that crops and groundwater in this area were fragile to soil heavy metals, especially Cd and Zn, because these two elements were very sensitive to acid rain.

Acknowledgements This work is partly financially supported by the cooperation project “Effects of acid deposition on chemical processes of soil heavy metals” (PRA E 00-04)

between Chinese and French scientists, and by the innovation foundation of Hunan Agricultural University (04PT02). Comments and constructive suggestions from two anonymous referees were very useful in preparation of the final version of this paper.

References

- Alumaa, P., Kirso, U., Petersell, V., & Steinnes, E. (2002). Sorption of toxic heavy metals to soil. *International Journal of Hygiene and Environmental Health*, 204(5–6), 375–376.
- Chao, T. T. (1972). Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Am. Proc.*, 36, 764–768.
- Fan, B. T. (1991). *Environmental chemistry* (pp. 388–390). Hangzhou: Zhejiang University Press.
- Gong, C., & Donahoe, R. J. (1997). An experimental study of heavy metal attenuation and mobility in sandy loam soils. *Applied Geochemistry*, 12(3), 243–254.
- Hernandez, L., Probst, A., Probst, J. L., & Ulrich, E. (2003). Heavy metals distribution in some French forest soils: Evidence for atmospheric contamination. *Science of the Total Environment*, 312, 195–219.
- Leleyter, L., & Probst, J. L. (1999). A new sequential extraction procedure for the speciation of particulate trace elements in river sediments. *International Journal of Environmental Analytical Chemistry*, 73(2), 109–128.
- Licskó, L. L., & Szebenyi, G. (1999). Tailings as a source of environmental pollution. *Water Science and Technology*, 39(10–11), 333–336.
- Liu, H., Probst, A., & Liao, B. (2005). Metal contamination in soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Science of the Total Environment*, 339(1–3), 153–166.
- Lu, R. K. (1999). *Analytical methods for soil agricultural chemistry (in Chinese)* (pp.24–26, pp.107–108, pp.206–213). Beijing: China Agricultural Science and Technology Press.
- Martínez, C. E., & Motto, H. L. (2000). Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*, 107(1), 153–158.
- Phillips, I. R. (1999). Copper, lead, cadmium, and zinc sorption by waterlogged and air-dry soil. *Journal of Soil Contamination*, 8(3), 343–364.
- Shuman, L. M. (1982). Division S-9-Soil Mineralogy: Separating soil iron- and manganese-oxide fractions for microelement analysis. *Soil Sci. Soc. Am. Proc.*, 46, 1099–1102.
- Strobel, B. W., Hansen, H. C. B., Borggaard, O. K., Andersen, M. K., & Raulund-Rasmussen, K. (2001). Cadmium and copper release kinetics in relation to afforestation of cultivated soil. *Geochimica et Cosmochimica Acta*, 65(8), 1233–1242.
- Tessier, A., Campbell, P. G., & Blason, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51, 844–851.
- Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M. R., Lofts, S., Hill, M. T. R., et al. (2003). The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environmental Pollution*, 125(2), 213–225.

- Wang, H. X. (2000). *Pollution Ecology (in Chinese)* (pp. 44–45). Beijing: Higher Education Press.
- Wilcke, W., & Kaupenjohann, M. (1998). Heavy metal distribution between soil aggregate core and surface fractions along gradients of deposition from the atmosphere. *Geoderma*, 83(1–2), 55–66.
- Wong, S. C., Li, X. D., Zhang, G., Qi, S. H., & Min, Y. S. (2002). Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environmental Pollution*, 119(1), 33–44.
- Wu, F., Wu, J., & Wang, X. (2000). The pollution characteristics of acid rain in Hunan Province. *Acta Scientiae Circumstantiae (in Chinese)*, 20(6), 807–809.

Modelling Change in Ground Vegetation Response to Acid and Nitrogen Pollution, Climate Change and Forest Management at in Sweden 1500–2100 A.D.

Harald Sverdrup · Salim Belyazid · Bengt Nihlgård · Lars Ericson

Received: 17 May 2005 / Accepted: 24 December 2006 / Published online: 14 March 2007
© Springer Science + Business Media B.V. 2007

Abstract The ForSAFE model, designed for modelling biogeochemical cycles (water, acidity, base cation, nitrogen and carbon) in terrestrial ecosystems, was modified with a vegetation response module (VEG), incorporating the effects of: nitrogen pollution, acidification, soil moisture, temperature, wind chill exposure, light and shading by trees, grazing by animals, competition between plants, above ground for light and below ground for water and nutrients. The model calculates the response of important ground vegetation plant groups. The integrated model was tested and validated at integrated level II forest monitoring sites across Sweden. Four are shown here, and are used to assess the effect of acidification and nitrogen pollution in relation to factors such as climate change, forest management and changing grazing pressure. The response functions have been derived from single-factor experiments

and integrated through the model structure for use on whole systems. The tests with the model suggest that the ground vegetation composition is reasonably well predicted, that much research remains before the model is fully tested and operational, and that the model may serve as a tool for assessing impacts of climate change, acid rain and forest management on plant biodiversity in forested areas.

Keywords ForSAFE model · Vegetation · Biodiversity · Soil · Climate change · Pollution

1 Introduction

Vegetation change and loss of plant species links to almost all environmental problems, and biodiversity has been given a high priority in the EU, defining a need for modeling of biodiversity aspects (EEA 1996; European Commission 1995; Grennfelt and Hov 2005; Grennfelt et al. 2001). Available evidence on several species shows a declining trend of diversity within ecosystems, habitats and among species in the EU (Green and Klomp 1996; Nilsson et al. 2005). Until present, the environmental effects originating from acid deposition, eutrophication and global climate change, have been investigated independently, because of lack of proper models. No models are yet available which will combine the effects of

H. Sverdrup (✉) · S. Belyazid
Chemical Engineering, Lund University, SE-221 00,
Lund, Sweden
e-mail: Harald.Sverdrup@chemeng.lth.se

B. Nihlgård
Plant Ecology and Systematics, Lund University,
SE-221 00, Lund, Sweden

L. Ericson
Genetics and Ecology, Umeå University, SE-901 87
Umeå, Sweden

climate change and deposition of sulfur and nitrogen using mechanistic approaches (Grennfelt and Hov 2005). The CLRTAP protocol will be reevaluated and revised during 2005, and models for predicting pollution impacts on biodiversity components can strengthen the case for stricter adherence to effects-based critical loads for multiple components of the ecosystems (Mapping Manual 2004).

2 Objectives and Scope

The focus of this study is modelling of ground vegetation and soil stocks of carbon, nitrogen and base cations in terrestrial ecosystems and how these changes with time as a result of pollution inputs, climate change and forest management. We want to use the model development process to build understanding of the vegetation dynamics and the feedback structures, study effects of (a) scenarios for future deposition of sulfur and nitrogen under implementation of the 1999 UN/ECE CLRTAP multi-pollutant protocol (b) climatic scenarios outlined by the IPCC and elaborated by the SWECLIM programme for Sweden (c) different forest or afforestation management scenarios in the Nordic countries. We also want to estimate critical loads based on ecological effects. The points above necessitates the development of an integrated model coupling acidity cycle, nitrogen cycle and the carbon cycle with forest management and growth. The model system is intended to provide decision support for environmental policy within Sweden as well as in LRTAP. This paper shows the first steps taken in to be able to reach such goals by the inclusion of a dynamic vegetation module to an existing cluster of biogeochemical models, ForSAFE.

3 Theory

3.1 Integrated Model Structure

Model components used here are all developed by different cooperating programmes with ForSAFE (Wallman et al. 2002); Soil chemistry, geochemistry, forest growth and production

(integrates biogeochemistry and soil processes, nitrogen/carbon cycle under managed forestry of tree size and age cohorts) and the ground vegetation response model VEG. The integrated ForSAFE–VEG model has the following ecosystem components:

- The tree vegetation layer
- The ground vegetation layer
- Nitrogen transformation processes
- The soil chemistry and geochemical processes
- The soil stocks and cycling of nutrients and carbon, including decomposition kinetics
- The hydrology

it calculates changes in present state at plot scale caused by physiochemical responses to ambient conditions and local competition at the site, and change in ambient habitat conditions due to biogeochemical processes. The existing biogeochemical component models have been independently validated and applied successfully in regional context (Aber et al. 1995; Akselsson et al. 2004; Alveteg et al. 1996, 1998; Barkman et al. 1996; Belyazid et al. 2005, 2006; Sverdrup and Warfvinge 1993a, b; Sverdrup et al. 1995, 1996; Warfvinge et al. 1992). In order to synthesize an integrated multiple stress system, ForSAFE–VEG (Fig. 1) provides simultaneous predictions of climate change, soil acidification and eutrophication with vegetation changes and effects on forest growth. ForSAFE has fully mechanistic nitrogen- and carbon-cycle submodels, and gives predictions of forest growth under production management (Stjernquist et al. 2002a, b; Svensson et al. 2002; Sverdrup et al. 2002; Wallman et al. 2002). Inside the soil chemistry and weathering box, the SAFE model is found. Inside the hydrology box, our version of the HBV/PULSE model, including a soil temperature submodule can be found. Inside the growth box, a modified PnET model can be found (Aber et al. 1995). The decomposition model is developed by Walse (1998) and Wallman et al. (2002). Inputs are deposition fluxes of S, N, base cations and water, plant uptake, climate parameters and soil properties, mineralogy alternatively weathering rate, some of these with vertical

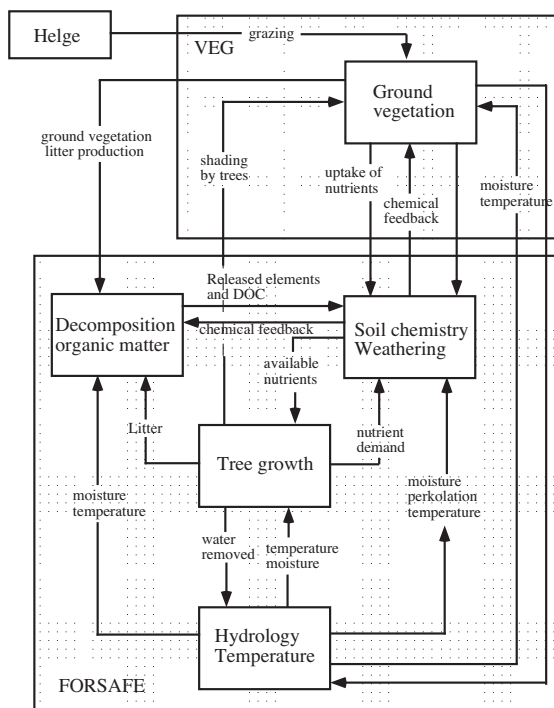
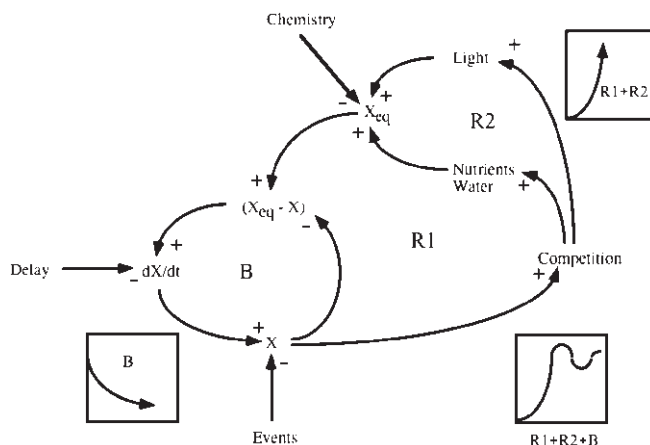


Fig. 1 Flow chart for the FORSAFE-VEG model is shown to the left. It shows how the different model components have been linked inside ForSAFE-VEG. A causal loop diagram of the process of change in the vegetation as represented by Eq. 1 is shown to the right. The diagram relates to the fraction of each plant group in the total vegetation composition. The loop marked *R1* and *R2* is a doubly reinforced loop, which with no limitation would



escalate (*R1+R2* part of the CLD diagram). It suggests that with little limitations, any plant group will fill the available niche, with competition it will rise to take the territory corresponding to its strength. The loop marked *B* is a balancing loop introduced by closing the gap between what territory it holds and what it can hold, this limiting effect (*B* part of the CLD diagram) prevents the reinforcing loop to escalate (*R1+R2+B* part of the CLD diagram)

resolution. Geochemical properties of the soil are important for determining the soil chemistry and the nutrient supply at sites. In ForSAFE, any number of soil layers may be used, but the normal configuration is to use four layers; one organic layer and three mineral layers. Outputs are soil chemistry, decomposition rates, mass fluxes and weathering rate per soil layer.

Table 1 The sites are covering a deposition and climatic gradient, S deposition ranges from 1.6 to 10 kg S ha⁻¹yr⁻¹ and N deposition from 2 to 18 kg N ha⁻¹yr⁻¹, the annual

Site name	Soil type	Vegetation	Sdep kg ha ⁻¹ yr ⁻¹	Ndep kg ha ⁻¹ yr ⁻¹
Brattfors	Haplic Arenosol	100% pine	1.6	2.0
Storulvsjön	Haplic Arenosol	100% spruce	2.3	3.5
Hensbacka	Haplic Podzol	93% spruce, 2% pine, 5% deciduous	10.0	18.0
Vång	Cambic Arenosol	97% spruce, 3% deciduous	9.0	17.0

3.2 The Main Equations

The change in vegetation composition state depends on two factors: The delay caused by survival of individuals in the population for a specific generation time τ . The change is also proportional to the driving force for change, the difference between what is there, the present system state

mean temperature varies from 0 to 7°C and precipitation from 0.7 to 1.3 m/yr

X , and what should have been if there were no delays, the immediate equilibrium state X_{Eq} . The principle has been illustrated in Fig. 1. The change in occupancy fraction X is found by combining these into the main equation:

$$\frac{dX}{dt} = \frac{1}{\tau} \cdot (X_{Eq} - X) \quad (1)$$

τ is the relaxation time of the particular plant group, used in Eq. 1 for delaying vegetation change. Once a plant group has become established at a site, there will be present a population of individuals with a certain life expectancy. Estimated relaxation times for each plant group has been listed in Table 2. Such factors as extreme drought or very low BC/Al ratios may shorten the delay time. The equilibrium occupancy fraction X_{Eq_i} of plant group i in the territory is estimated by using an equation based on competition strength (S):

$$X_{Eq_i} = \frac{S_i}{\sum_{i=1}^{i=species} S_i} \quad (2)$$

where X_{Eq_i} is the fraction of the territory occupied at equilibrium with the site state parameters, S_i is the individual strength of plant group i at each instant as determined by the site state parameters, the total plant group strength with which it measures itself in the competition for land occupancy. The ground vegetation composition in a forest or a field is determined by a number of parameters:

1. Promoting and retarding effects of soil solution nitrogen
2. Light reaching the ground
3. Soil water
4. Effect of temperature including wind chill
5. Plant community competition
 - (a) above-ground geometry for mutual shading and competition for light
 - (b) below-ground geometry for nutrients, water and exposure to chemistry
6. effect of soil chemistry, in particular soil solution acidity
7. grazing and browsing
8. forest fires
9. Forest management, thinnings, harvest, clearing, planting

For any plant i the individual strength is given by the product of strengths derived from nutrients, strategies and conditions:

$$S = f(Nutrient) \cdot f(Water) \cdot f(Acid) \cdot f(Grazing) \cdot f(Temp) \cdot f(Wind) \cdot f(Light) \quad (3)$$

Depending on changes in site conditions, the amounts of ground vegetation and its composition will change. The intensity of the conditions rather than mass fluxes will determine the conditions. Competition strategy is how competition for the resources and the avoidance of retarders is done by each plant group. The community composition trajectory through time can be calculated when all such systems for each plant group present are let to dynamically interact in a mathematical model. $f(Acid)$ is the soil acidity response function, $f(Nutrient)$ is the nitrogen response function, $f(Water)$ is the soil moisture function caused by water saturation and exclusion of air from the soil, $f(Light)$ is the response function depending on the amount of light coming to the ground. The maximum amount of light $f(Light)$ is reduced with any occurring shading from trees, as well as the reduction in intensity that occurs as one moves north. Light in excess of the maximum plant capacity has no effect. $f(Temp)$ is the effect of temperature, $f(Wind)$ is wind chill that act on the temperature and separately by flag tatter at sites exposed to strong winds. $f(Grazing)$ is the effect of grazing by animals. It is a preferential reduction of above ground plant size and affects competition.

At present, the effects of gaseous pollutants have been omitted. The response functions are all scaled between 0 and 1, where 1 represents the state of no-effect from that factor. All the responses have the basic form of a promoting part and sometimes a retarding part. These are either expressed as parametric mathematical forms or as diagrams. For some plants and some parameters, there is no retarding functions. The above ground competition strategy of the plant for capturing light and preventing others from getting it, is depending on plant height and its shading capacity. The root competition strategy for capturing water and nutrients, as well as exposure to pH and BC/Al in acid soils, is expressed through root

Table 2 Parameterization of ForSAFE–VEG, Sweden

Latin name	τ	[N]	[H ⁺]				W			T			I			h	root	k _P	k _G			
			X	a ₀	k+	w+	k-	w-	k _{BC/AI}	k(pH)	k _{BC}	min		top						max		
												min	top	min	top							
	ys																					
Cladonia lichen	20	a	1	0.01	1	0.003	3	0.07	1,050	0	-0.20	0.05	0.25	-2.5	5.5	13.5	100	500	0.05	0	0.1	0.7
Hylocomium mosses	20	b	1	0.03	1	-	-	0.07	1,050	1.5·10 ⁵	0.05	0.15	0.35	-1	7	15	20	500	0.02	0	3	0
Mnium mosses	20	f	1	0.3	2	-	-	0.4	6,000	0	0.15	0.25	0.60	0	8	16	10	500	0.02	0	3	0
Sphagnum mosses	20	b	1	0.03	1	0.1	3	0.01	150	1.5·10 ⁵	0.40	0.60	1.00	-1	7	15	20	500	0.02	0	1	0
Calluna vulgaris	30	e	1.4	0.2	1	3	3	0.2	3,000	0	-0.25	0.15	0.40	-1	7	15	100	1,000	0.25	2	1	0.7
Empetrum nigrum	15	b	1.6	0.03	1	0.003	3	0.2	3,000	1.5·10 ⁵	-0.20	0.10	0.40	-1.5	6.5	14	150	1,000	0.10	1	1	0
Erica tetralix	15	f	1.6	0.3	1	0.03	3	0.4	6,000	0	0.20	0.35	0.60	0	8	16	200	1,000	0.15	1	1	0
Vaccinium myrtillus	10	d	1.6	0.1	1	0.1	3	0.1	1,500	0	-0.10	0.15	0.50	-1	5	11	50	500	0.30	1	1	2.3
Vaccinium vitis-idea	15	b	1.6	0.03	1	0.003	3	0.35	5,250	0	-0.20	0.10	0.45	-1.5	4.5	10.5	100	800	0.15	1	1	0.7
Agrostis capillaris	5	2.5	1	0.5	2	-	-	0.2	3,000	0	0.05	0.15	0.50	3	11	19	150	800	0.25	2	3	2.3
Brachypodium pinnatum	5	5	1	20	2	-	-	6	3,500	0	0.10	0.20	0.35	3	11	19	200	700	0.50	1	3	9
Bromus benekenii	5	5	1	20	2	-	-	12	180,000	0	0.10	0.20	0.40	5	13	21	50	600	0.60	2	30	9
Calamagrostis arundinacea	5	2.5	1	0.5	2	-	-	1.8	20,800	0	0.10	0.20	0.40	2	10	18	150	700	0.50	2	3	0.7
Deschampsia cespitosa	5	2.5	1	0.5	2	-	-	0.2	3,000	0	0.15	0.35	0.60	3	11	19	200	1,000	0.35	2	3	0
Deschampsia flexuosa	5	1	1	0.05	2	-	-	0.13	1,950	0	0.05	0.15	0.30	-1	7	15	50	600	0.20	2	3	2.3
Festuca ovina	10	1	1.4	0.02	2	10	1	0.1	1,500	0	-0.25	0.05	0.25	3	11	19	300	1,000	0.10	1	30	0.7
Milium effusum	5	5	1	20	2	-	-	8	150,000	0	0.15	0.45	0.60	5	15	20	50	600	0.50	2	3	9
Molinia caerulea	5	3	1	1	2	-	-	0.2	3,000	0	0.20	0.30	0.45	5	13	21	200	1,100	0.40	2	30	2.3
Nardus stricta	10	1	1.2	0.05	2	10	1	0.2	3,000	1.5·10 ⁵	0.15	0.25	0.40	0	8	16	300	1,000	0.15	2	1	0
Poa nemoralis	5	4	1	5	2	-	-	8	120,000	0	0.05	0.10	0.20	2	10	20	250	1,000	0.40	2	3	9
Dryopteris dilatata coll	20	2.5	1	0.5	2	-	-	2	30,000	0	0.15	0.30	0.50	3	11	16	30	500	0.50	2	1	2.3
Pteridium aquilinum	20	2.5	1	0.5	2	-	-	0.2	3,000	0	0.05	0.20	0.30	2	8	18	150	650	0.70	2	1	0
Aconitum lycoctonum	20	2.5	1	0.5	2	-	-	10	150,000	0	0.15	0.45	0.90	2	10	14	50	1,000	0.50	2	1	0
Allium ursinum	2	5	1	20	2	-	-	40	600,000	0	0.25	0.40	0.60	4	12	20	50	1,000	0.25	2	30	0
Anemone nemorosa	10	2	1	0.5	2	-	-	0.8	12,000	0	0.20	0.30	0.40	2	10	18	50	700	0.15	1	3	2.3
Antennaria dioica	5	1	1	0.01	2	-	-	0.1	1,500	0	0.05	0.10	0.20	0	6	12	400	1,100	0.01	1	1	0
Arnica montana	5	1	1	0.01	2	-	-	0.6	9,000	0	0.05	0.10	0.20	7	15	20	400	1,100	0.02	1	1	0
Epilobium angustifolium	5	3	1	1	2	-	-	2	30,000	0	0.15	0.20	0.30	0	8	20	350	1,100	0.50	2	3	32

Table 2 continued

Latin name	τ	[N]	[H ⁺]			W			T			I			h	root	k _P	k _G					
			X	a ₀	k+	w+	k-	w-	k _{BC/Al}	k(pH)	k _{BC}	min	top	max					min	top	max	min	sat
Galium odoratum	3	4	1	5	2	-	-	-	1.2	18,000	0	0.15	0.25	0.40	3	11	19	50	600	0.15	1	1	0.7
Geranium sylvaticum	3	3	1	1	2	-	-	-	1.8	27,000	0	0.15	0.25	0.40	2	10	14	100	600	0.50	2	3	9
Hepatica nobilis	20	3	1	1	2	-	-	-	8	120,000	0	0.15	0.25	0.40	2	10	18	75	600	0.20	1	3	0
Mercurialis perennis	5	4	1	5	2	-	-	-	2	30,000	0	0.10	0.25	0.40	5	15	20	200	1,000	0.50	1	1	0
Origanum vulgare	20	2	1	0.5	2	30	1	10	150,000	0	0.05	0.15	0.25	0.40	4	12	20	300	1,200	0.05	2	3	0.7
Oxalis acetocella	2	2.5	1	0.5	2	-	-	-	0.2	3,000	0	0.10	0.20	0.40	0	8	18	50	600	0.05	1	1	0
Trifolialis europaea	2	2.5	1	0.5	2	10	1	0.2	3,000	0	0.10	0.20	0.40	0.2	10	18	50	600	0.15	1	1	0.7	
Trifolium repens	5	-	1	1	0	-	-	-	1.3	19,500	0	0.20	0.35	0.40	5	12	18	250	1,100	0.30	2	1	32
Urtica dioica	5	4	1	5	2	-	-	-	10	150,000	0	0.15	0.25	0.45	2	10	20	100	1,000	0.50	1	3	0
Norway spruce	100	1	1	0.3	2	30	1	0.33	5,000	0	0.10	0.4	0.9	0.9	5	15	20	100	175	0.25	1	3	0.7
Sitka spruce	110	0.5	1	0.1	2	3	1	0.07	1,050	0	0.15	0.45	0.9	0.9	2	12	17	150	175	0.25	1	1	0.7
Scots pine	150	3	1	1	2	100	1	0.28	4,730	0	0.05	0.3	0.8	0.8	3	13	18	300	574	0.20	2	1	0.7
Larch	70	3	1	1	2	30	1	0.5	6,000	0	0.05	0.25	0.8	0.8	6	16	25	100	175	0.20	2	3	0.7
Birch	60	3	1	1	2	100	1	0.25	4,000	0	0.15	0.45	0.9	0.9	2	12	17	200	400	0.20	2	1	9
Beech	120	4	1	3	2	300	1	0.22	3,500	0	0.15	0.45	0.7	0.7	6	16	30	80	150	0.25	3	3	2.3
Oak	160	4	1	3	2	300	1	0.2	3,000	0	0.05	0.3	0.7	0.7	6.5	16.5	35	150	200	0.2	3	3	9
Ash	80	3	1	1	2	-	-	-	0.25	4,000	0	0.15	0.45	0.7	7	17	35	150	400	0.25	2	3	9
Maple	80	4	1	3	2	-	-	-	0.25	4,000	0	0.05	0.3	0.7	5.5	15.5	25	40	70	0.20	3	3	9
Myrica gale	10	-	1	1	0	-	-	-	0.8	12,000	0	0.25	0.35	0.60	3	7	18	300	800	0.30	2	1	0.7
Rhododendron toment	10	1.5	1	0.03	2	3	3	0.2	3,000	1.5·10 ⁵	0	0.25	0.35	0.5	-1	5	9	200	700	0.25	2	1	0
Rubus idaeus	5	3	1	1	2	-	-	-	1	15,000	0	0.15	0.25	0.40	2	10	18	300	1,000	0.50	2	3	9
Salix lanata	30	2.5	2	0.05	1	0.1	3	0.6	9,000	0	0.15	0.35	0.60	-2	3	7	150	800	1.0	3	1	2.3	
Salix myrsinifolia	30	2	1	0.5	2	-	-	-	0.5	9,000	0	0.25	0.40	0.60	-1	5	11	200	800	1.20	3	1	9

τ the delay time in years, X is nitrogen class, [N] is nitrogen, [H⁺] is soil acidity, Temperature T in °C. I is light in $\mu\text{mol photons m}^{-2}\text{s}^{-1}$, h effective plant height in meter, W is soil moisture in m^3 water per m^3 soil. *min* is where growth starts, *top* is where the maximum is reached, *max* is where the retardation starts.

distribution in different soil depths. Competition strategy is not a separable function, but acts indirectly. When roots are present in several soil layers, the root weight weighted average of the functional value is used.

$$f = \sum_{i=1}^{\text{rooted layers}} x_i^{\text{root}} \cdot f_i \quad (4)$$

where f is the response function for the site condition being responded to. We need to make the following assumptions for this: (1) The effects are separable and independent inside the plant species (2) Feedbacks between the driving variables occur only on the soil biochemistry side (3) The effects are multiplicative and mutually compensating.

3.3 Individual Parameter Responses

For light, temperature, water and phosphorus a generic response curve was adopted (Fig. 2), and all response function coefficients can be found in Table 2. The shape was derived by generalization of response descriptions (Hansson 1995; Lambers et al. 1998; Latour et al. 1994; Tilman 1994). Important for the nitrogen, light and water responses are the effect of trees in the forest stand, which have the capacity to remove large amounts of nitrogen, water and light. The basic shape of the temperature, light and soil moisture response function is shown in Fig. 2. The function is applied in every soil layer for moisture, nutrients, the light function to the irradiation down to the ground vegetation, the temperature function to the whole plant body. The start ($x_{\min}$), first bend (x_{top}) and second bend ($x_{\max}$) are all defined and given in Table 2. Threshold values are necessary, below the threshold, no effect, above, there is effect. The parameters have been derived by a reinterpretation of the results of Ellenberg (1992), Falkengren-Grerup 1992 and Bobbink et al. (2002) as well as many studies compiled and used by them, many unpublished studies and a Delphi process involving interviewing specialists in the field for accessing unpublished data. Two of the authors (Ericson and Nihlgård) have access to the data archives of their respective ecology institutions, providing access to data and information that is

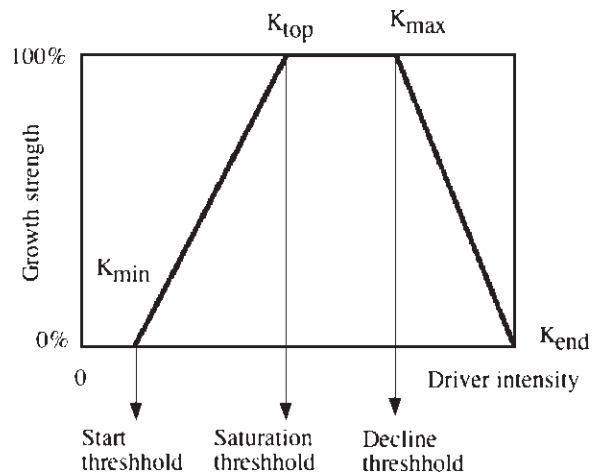


Fig. 2 The basic shape of the temperature, light and soil moisture response function follow the shape of the Michaelis–Menten equation. The function is applied in every soil layer for moisture, nutrients, the light function to the irradiation down to the ground vegetation, the temperature function to the whole plant body

physically available there, but unfortunately will remain unpublished in the foreseeable future.

3.3.1 Nitrogen

The nitrogen response depend on soil solution nitrogen. The plant can only observe the chemical activity of soil solution, and not the contents in solids. Nitrate enters the plant with the water flux, ammonium enters the plant through water uptake, as well as actively through the same mechanism as potassium. Nitrogen response has shown two major types. One type of response which first increases at low nitrogen availability, and a second type of response which retards the plant group at higher concentrations, when nitrogen is in excess. The decline can be caused by different processes, such as promotion of parasites (fungi, bacteria, insects, large herbivores) or toxic effect of ammonia.

$$f(\text{Nutrient}) = a_0 \cdot \left(\frac{[N]^{w_+}}{k_+ + [N]^{w_+}} \right) \cdot \left(\frac{k_-}{k_- + [N]^{w_-}} \right) \quad (5)$$

The equations for the promotive effect form the first part, the retarding effect is caused by high nitrogen content which makes the plant desirable for predators and pathogens. Phosphorus is also involved, but since it does not play a prominent

role at present, it has been omitted here. For plant groups where only qualitative information is available, we have qualitatively ranked the plants. Researchers have shown that this effect is most likely the effect of parasites and pathogens (Nordin et al. 2004; Strengbom et al. 2002). In particular for blueberry (*Vaccinium myrtillus*), but probably also for cranberry (*Vaccinium vitis-idea*) and heather (*Calluna vulgaris*), they could show that the fungus *Valdensia* was active and its attack was promoted by nitrogen availability to the plants.

3.3.2 Soil Chemistry

The response to soil acidity derives from the effect of low soil solution pH and the high soil solution concentrations of Al^{3+} associated with soil solution acidity. In the model, we have adopted the minimum of the pH and the BC/Al response functions, because in the top layers, Al^{3+} will often be complexed with organic acids and have no or little effect on plants. In lower layers, a smaller fraction of Al^{3+} will be complexed and the effect of Al as expressed by the BC/Al function will have larger impact than the H^+ -ion alone: They are applied as follows in each layer where they have roots:

$$f(\text{Acid}) = \min \left(f \left(\frac{\text{BC}}{\text{Al}} \right), f(\text{pH}) \right) \cdot f(\text{BC}) \cdot f(\text{pOH}) \quad (6)$$

This will have the following practical implications: For the organic layer in the top of the profile, the response function based on soil solution pH will be most important for plant impact. For the mineral layer below the organic layer, both the pH and the BC/Al function may be of importance. For plant impact, only the BC/Al function will be important. The impact of acidity is calculated from a principle, which was first discovered by Ulrich (1985) as a concept based on the soil solution calcium to aluminium ratio, and later theoretically elaborated and enhanced by Sverdrup and Warfvinge (1993a, b). This was done by application of root exchange and uptake molecular mechanisms to include: H^+ , BC^{2+} and Al^{3+} in experimentally determined response isotherms. The ensuing formula has the shape of a Michaelis-menten formula, consistent with the Barber

equation for Ca and Mg uptake in crop plants and mechanisms suggested by Marschner (1991, 1997). The coefficient $k_{\text{acid},i}$, where i is plant species, can be found tabulated for approximately 100 different plants, based on a synthesis of nearly 300 experiments on plants all over the world (Sverdrup and Warfving 1993a, b). This parameter was adapted by the UN/ECE as the key parameter for setting critical loads for acid deposition to terrestrial systems. For all the plant groups, we have simplified the expression to:

$$f \left(\frac{\text{BC}}{\text{Al}} \right) = \frac{\frac{[\text{BC}]}{[\text{Al}]}}{k_{\text{BC/Al}_i} + \frac{[\text{BC}]}{[\text{Al}]}} \quad (7)$$

If we choose to work with $\text{pH}(\text{H}_2\text{O})$ only, the simplified response expression becomes:

$$f(\text{pH}) = \frac{1}{1 + k_{\text{pH}_i} \cdot [\text{H}^+]} \quad (8)$$

This formula inherently assumes constant base cation concentration and a uniform relationship between H^+ and Al^{3+} everywhere. Some of the plants on our list are calcifuge, they cannot stand high solution concentrations of calcium. Functions for decline at high pH, $f(\text{pOH})$, and calcifugicity, $f(\text{BC})$, are also included in the model. For wild plants and trees, only a few field experiments on mature plants are available. These are, however, consistent with the laboratory experiments, suggesting that laboratory experiments are applicable to mature plants. Mycorrhiza on spruce and pine show the same response to acidity as the host tree (Sverdrup and Warfving 1993a, b). Some plants on our list show symptoms of problems with their Mg and P uptake at high concentration of base cations. They cannot tolerate high concentrations of Ca in the soil solution for Mg and P uptake, and Ca and Mg in the soil solution for P uptake (Larcher 1975–1995).

3.3.3 Moisture

The plants depend on soil moisture for water uptake and it is also required for soil processes like ion exchange, weathering and decomposition to function. Response curves are available for some trees and a few crop plants, but for the rest only descriptive information is available (Sverdrup

et al. 2002). Water response functions have been derived by using commercial gardening trade handbooks, the general flora for the Nordic countries (Mossberg and Stenberg 1997) and field surveys by one and each of the authors in terrestrial ecosystems in Norway and Sweden. The dependence on soil moisture, follow the shape shown in Fig. 2. At very high soil moisture, air is excluded and the plant will not grow. When drought is persisting below the lower limit for a plant for more than one growth season, the plant cover is reduced instantly, regardless of a long generation time. The ranges of the some plants were found in such terms, and the others were ranked among them. For some plants, important modifications must be considered: *Cladonia* species can tolerate prolonged and severe drought without any significant effect. The *Vaccinium vitis-idea*, *Calluna vulgaris* and *Festuca ovina* groups can tolerate seasonal drought without significant increase in mortality. These plants will be favoured at sites exposed to repeated drought and severe water stress.

3.3.4 Temperature and Wind Chill Effects

The temperature range was set for each plant group, following the shape defined in Fig. 2, with temperature as input. At sites on open land or with such tree cover that the ground surface is exposed to the wind, the wind-exposed ground vegetation suffers from lowering of the physiological temperature by the wind chill effect. This effect lowers the temperature with increasing wind speed (Guyot 1998). This limits plants and trees in occupying wind-exposed sites in the landscape. The temperature affecting the physiological functions of the plant is decreased. In forested stands, especially evergreen conifer stands, the wind effect will normally be negligible, on forest edges of natural or management origin, in regions close to the natural tree-line, or due to topography, the effect may be significant enough to prevent rejuvenation of forest and affect ground vegetation significantly. The wind velocity felt for a specific plant depend on its height h and the actual wind velocity felt by the plant. The stagnant layer thickness depend on landscape roughness and fine-scale topography. High plants will have

a strong disadvantage in windblown landscapes. The height represents the effective height of the plant leaves, the essential part for photosynthesis and survival.

3.4 Competition, Light and Roots

There are two ways of competing. One is for light above ground, the other is for nutrients and water (Hanks and Ritchie 1991; Marschner 1997; Tillman 1994). Since the plant uses the same apparatus for water and soil nutrients, different strategies are possible, depending on whether emphasis is put on water or nutrients and on whether the plant needs a fast strategy or a long term strategy. A function as shown in Fig. 2 applies to the effect of light supply on the plant, $f(\text{Light})$, with a threshold value where the plant initializes growth and a maximum capacity where light has no further effect. Landuse and management affects available light reaching the ground and by thinning the forest cover or changing it to open land. Many plants require a minimum light amount to start, as indicated in the parameter list. Light to the ground vegetation is limited in three ways:

1. Latitude of the geographical location and the yearly season,
2. Shading by trees and bushes
3. Shading from other ground vegetation species

Shading from trees is produced internally in the ForSAFE model. The light availability at the geographical location is given by the longitude and latitude, and the shading by other competitors on the ground by the above ground competition parameter. Threshold values are necessary, below the threshold, no effect, above, there is effect. The equations for a single plant describing how much light I_i , it can capture and how this is related to the leaf area index, (LAI), is according to the Lambert–Beer Extinction Law (Kimmins 1996; Larcher 1975–1995). The Lambert–Beer law implies that light decrease exponentially with distance from the top of the forest canopy. This is equivalent with the light extinction degree being exponentially dependent on vegetation height. The effect of trees on the amount of light reaching

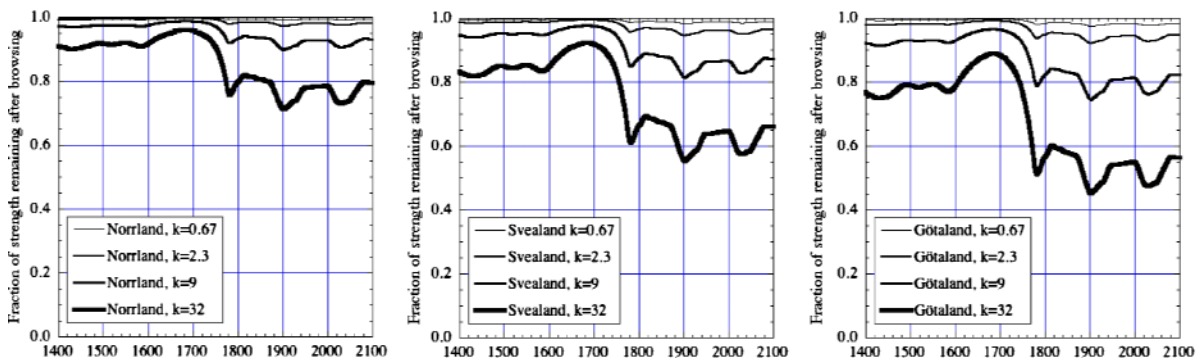


Fig. 3 Calculated grazing pressure for the four different impact classes using the Hälge model and the specific grazing response functions. This was used as input to the ForSAFE-VEG model in the runs presented here

the ground is given by Eq. 9. The limits for light have been expressed in $\mu\text{mol photons m}^{-2}\text{s}^{-1}$.

$$f(\text{Light}) = 0.65 \cdot e^{-3.08 \cdot X_{LAI}} \quad (9)$$

X_{LAI} is the fraction of maximum leaf area index (LAI) for Norway spruce in Sweden. A major component of competition is for light. The plants shade each other and thereby transfer a disadvantage. The ground vegetation plants shade each other according to Eq. 10:

$$f(\text{Shade}) = 0.0273 \cdot e^{\beta \cdot h} \quad (10)$$

where h is effective plant height for competing for light. This is not the same as the maximum height of the plant, it is rather the height reached by the bulk of the leaf mass that will be able to provide shadow on competitors. β in the exponent

is the shape factor, we have set $\beta=3$ consistently for all plants. The only occasion when the ground vegetation has a feedback on the tree population is when the trees are in the seedling stage. Then the shading will follow the expression given in Eq. 10. Below ground competition is expressed by the rooting depth and layer distribution of root mass. It is not a separable function, but rather inherent in the model structure and the fact that the model operates in several soil layers. We have adopted four different rooting patterns that form the basis of our classification. Classification was used because exact measurements are normally not available, but a lot of empirical undocumented experience can be used for fairly secure classification. For these variables, the class constants were assigned to each species. Below ground competition is expressed through which soil layers the plant is exposed to the driving variables, and the layer by layer effect is averaged.

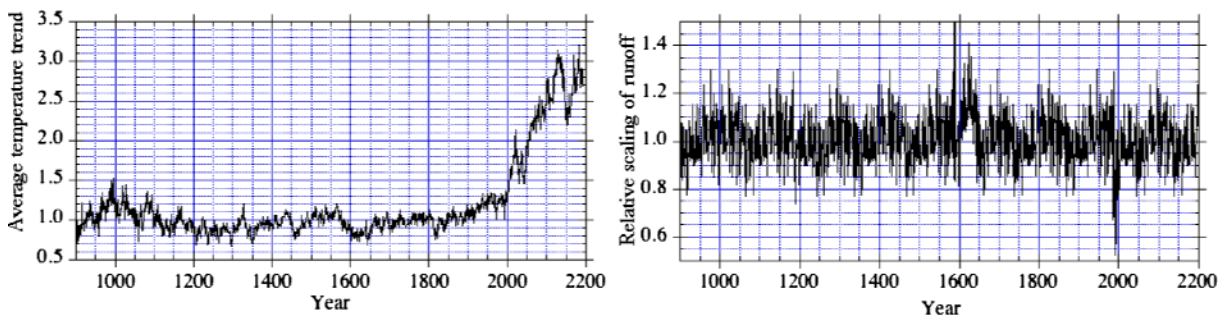


Fig. 4 Inputs to the runs presented. Trends for temperature taken from the IPCC 2001 historical reconstruction since 831 A.D. to 1900 as well as the standard IPCC scenario

for the period 1900–2300. Trends for annual water flow variations for the time period 831–2250 (Climate Change 2001, the scientific basis, IPCC)

■ Cladonia_lichen	■ Hylocomium_mosses	■ Mnium_mosses	■ Sphagnum_moss
■ Calluna_vulgaris	■ Empetrum_nigrum	■ Erica_tetralix	■ Vaccinium_myrtillus
■ Vaccinium_vitis-idea	■ Agrostis_capillaries	■ Brachiopodium_pennatum	■ Bromus_benekeii
■ Calamagrostis_arundinasius	■ Deschampsia_cespitosa	■ Deschampsia_flexuosa	■ Festuca_ovina
■ Milium_effusum	■ Molinia_caerulea	■ Nardus_stricta	■ Poa_nemoralis
■ Dryopteris_dilatata_coll	■ Pteridium	■ Aconitum_lycoctonum	■ Allium_ursinum
■ Anemone_nemorosa	■ Antennaria_dioica	■ Arnica_montana	■ Epilobium_augustifolium
■ Galium_odorata	■ Geranium_sylvestrum	■ Hepatica_nobilis	■ Mercurialis_perennis
■ Origanum_vulgare	■ Oxalis_acetocella	■ Trientalis	■ Trifolium_repens
■ Urtica_dioica	■ Myrica_gale	■ Rhododendron_toment	■ Rubus_idaeus
■ Salix_lanata	■ Salix_myrsinifolia		

Fig. 5 The plant groups used and their code in the plots

3.5 Browsing and Grazing by Ungulates and Livestock

Grazing pressure is important for ground vegetation competition, forest structure and should be included in any ground vegetation model applied in areas where herbivores are present in significant numbers. A separate ungulate model was built (HÄLGE), and it was used to estimate average grazing pressure over time as input to ForSAFE-VEG. Considered were ungulates, sheep and cattle in the Hälge model, the population depend on forage, predators and hunting. The Hälge model has the following components: Moose population: calf, cow, old, Conifer forest: Seedlings, young trees, mature trees, old growth, Deciduous forest: Seedlings, young trees, mature trees, old growth, Grass forage: Ground vegetation under deciduous forest, ground vegetation under coniferous forest. The grazing unit is moose units. One moose unit corresponds to 300 kg live weight of animal regardless of size and species. Of the Swedish sites used for model tests, we chose to show Brattfors, Storulvsjön in the Norrland region, Hensbacka in the Svealand region and Vång in the Götaland region. Each class represents how much a plant is impacted by the animals, grazing and trampling. The grazing pressure for the individual plant group is:

$$f(\text{Grazing}) = \frac{1}{1 + k_G \cdot d} \quad (11)$$

where d is the animal density in moose units per km^2 . The factor $f(G)$ for each plant will vary between zero and 1.0. The density of animals in the

territory has during the last recorded history, varied too much over time to be represented by a fixed average. The elimination of predators, the restructuring of the forest, changes in hunting pressures and the observed changes in climate have all



Fig. 6 Map of the total number of sites used in the study, four of them are treated in this report

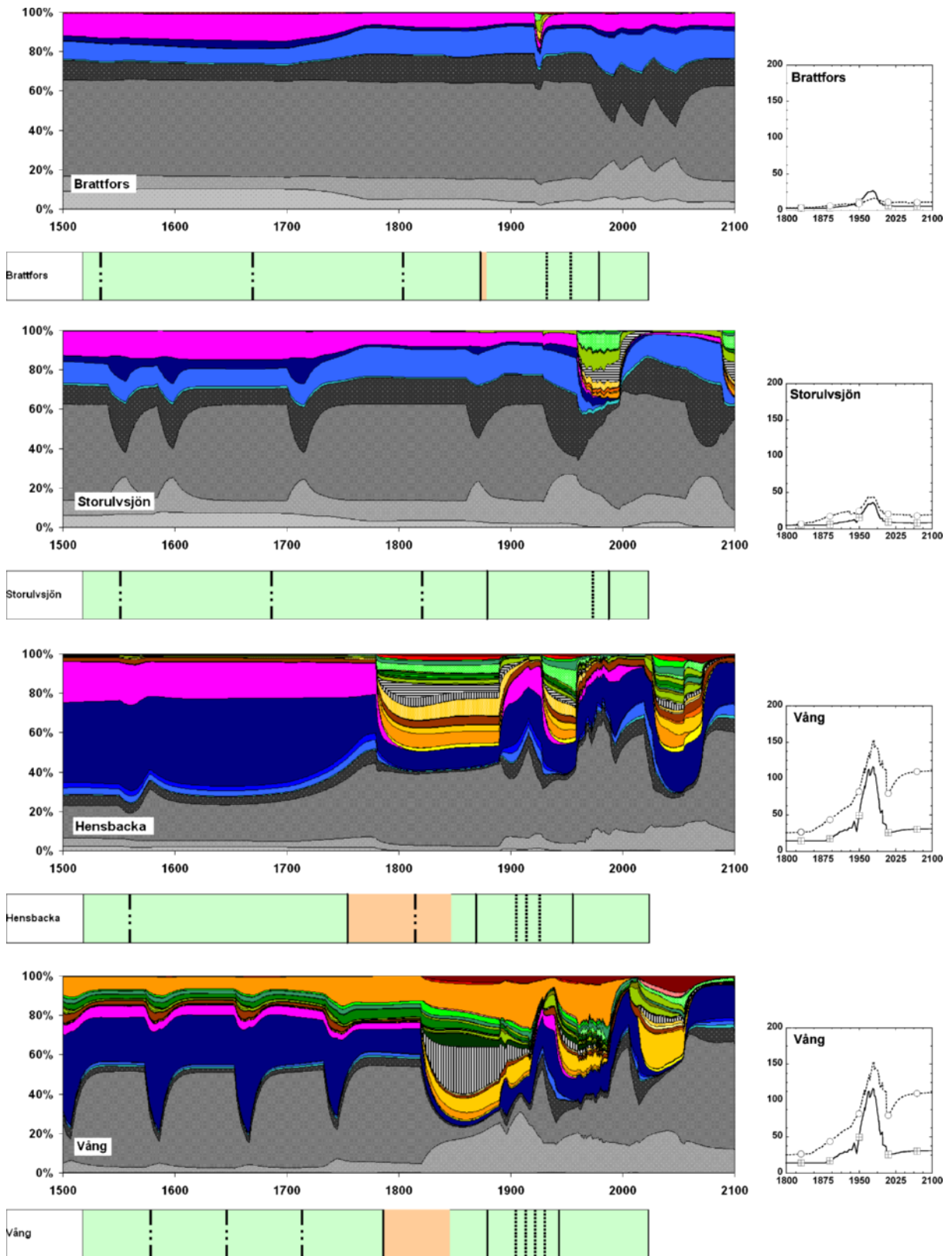


Fig. 7 Ground vegetation composition simulation results for the period 1500–2100, from *top left*: Brattfors, Storulvsjön, Hensbacka and Vång. *Under each picture*, the management history has been shown. A *dashed line* is a forest fire, a *straight line* is a clearcut, *stipled lines* are thinnings in the stand. The *orange shaded field* is a period with open land and grazing. To the *right*, the development of deposition of sulphur (*red*) and nitrogen (*blue*)

contributed to changes. Grazing stimulates growth by removing self-shadowing and competitors.

3.6 Primary Biomass Production by Grass

Ground vegetation and in particular grass will have a primary production of biomass, depending on nutrients and light. A basic grass production rate is calculated according to an equation adapted after Fridriksson and Sigurdsson (1983) and Bergthorsson (1985), generalized for Scandinavia. If we take the effect of soil moisture, pH and light into account, the ground vegetation Net Production (NP) is given by:

$$r_{NP} = \alpha \cdot (0.4 + 0.2 \cdot T - 0.01 \cdot T^2) \cdot (2.5 + 4.9 \cdot 10^6 \cdot [N] - 2.2 \cdot 10^9 \cdot [N]^2) \cdot f(\text{Water}) \cdot f(\text{Light}) \cdot f(\text{pH}) \quad (12)$$

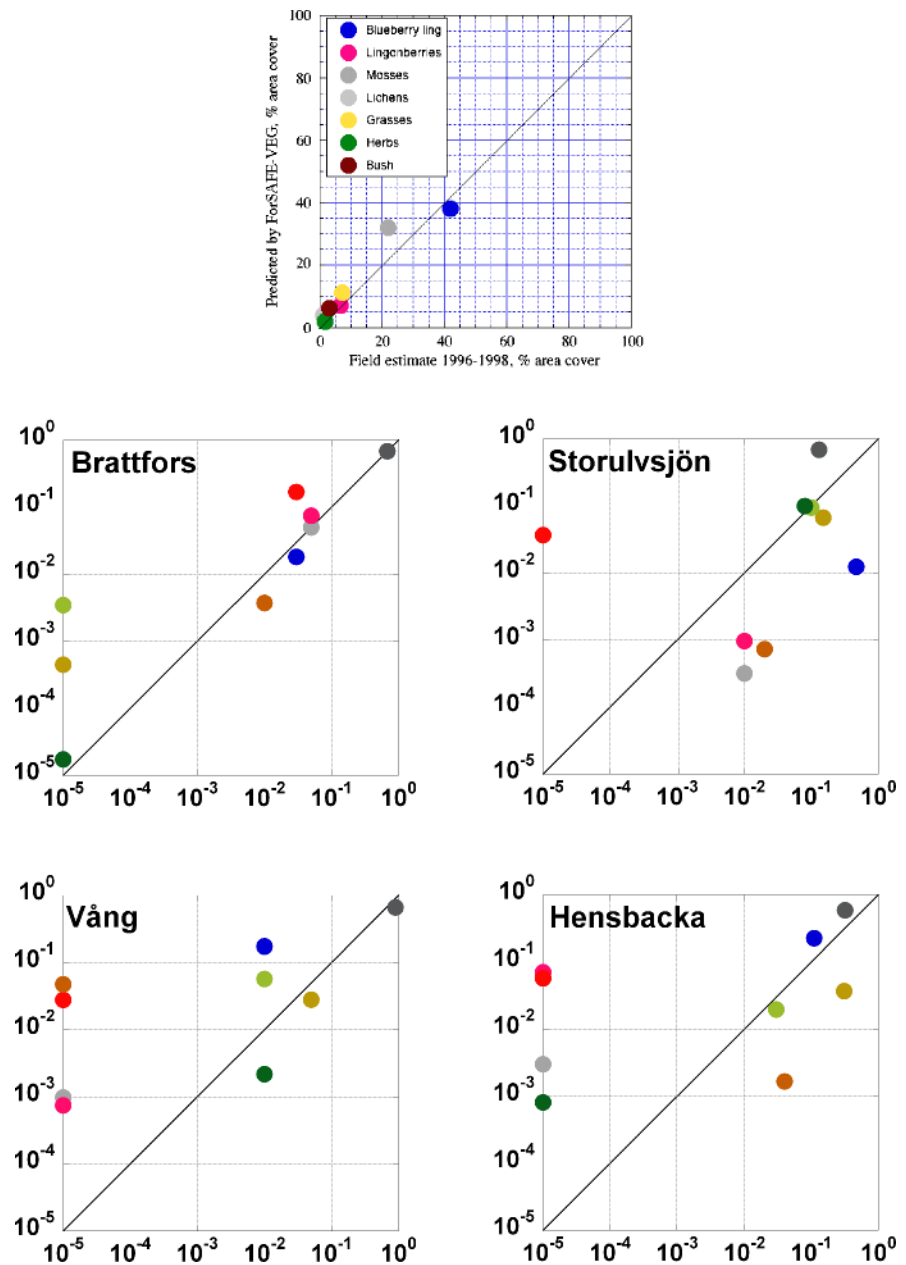
The net production of grassy vegetation is expressed in kg biomass ha⁻¹yr⁻¹. [N] is the soil solution concentration (kmol m⁻³) of nitrogen, and Q the percolation rate at the bottom of the root zone, why Q · [N] will give units of kg N ha⁻¹yr⁻¹. f(Light) is the shading function by trees, f(Acid) the soil solution acidity, and f(Water) the soil moisture. α is a constant fitted once to average grass production in Sweden, and held constant. The grass production causes an uptake during the season depending on primary production, corresponding to a C/N ratio in the grass of 20. Of the grass production, all above-ground grass was set to die every year, and returned with litterfall. Of the below ground biomass produced, below ground production amounts to 0.4 times the above ground amounts. Of this, an amount comparable to the newly grown grass biomass becomes litterfall every year. We assume that the ground vegetation biomass stock reaches steady state within a year, dead grass in litterfall is added to the soil

organic matter stock and decomposed with that material. Under a forest, the grass production will be limited by nitrogen availability and light to almost negligible biomass amounts, however during clear-cuts and on open land, this is important for maintaining soil carbon and nitrogen stocks.

4 Input Data and Parameters

We have identified different indicator plants associated to an equal number of functional plant groups and several indicator tree species for different parts of the Scandinavian area. In addition, earthworms were selected because of their special function and as data for them where available. These are the indicator plants for each of the 42 ground vegetation plant functional groups. All other plants added to the model are added to one of these 42 groups and to nine Swedish stand forming tree species. Trends for temperature and water flow variations for the time period from 831 to 2250 A.D., partly as taken from the standard IPCC scenario for the period 1900–2300 are shown in Fig. 4 (IPCC 2001). The curves are normalized variation curves, based on the base year 1900. Before 1820, forest harvest was occasional and small in volume at all sites. Forest fires were included as inputs to the model, as shown in the results together with landuse history. They are dependent on how moist the climate and soil in the area is, and the frequency of lightning and careless humans. In a typical forest fire, 40% of the wood in the trees will be incinerated, returning 40% of the carbon and 60% of the nitrogen to the air. The rest of nitrogen and carbon becomes litterfall. 80% of the base cations in the burned biomass is released to the soil solution. Of the above ground vegetation, 80% will be incinerated, carbon and nitrogen gasified, base cations released to the soil solution, and the rest given to litterfall. Figure 3 shows the calculated grazing pressure for the four different impact classes using the Hälge model and the specific grazing response functions. Each plant group has been assigned either one impact class or the no-impact class for grazing. The grazing class include grazing of ground vegetation, browsing on bushes and trees as well as effects of trampling (Figs. 4, 5 and 6).

Fig. 8 Validation of the FORSAFE-VEG model using input data from Svartberget with detailed site data of good accuracy. For Brattfors, Storulvsjön, Hensbacka and Vång, generalized input data from forest inventories and regional assessments were used. Svartberget and Brattfors are in close proximity and comparable sites, and may be used to illustrate what happens when we change from site specific, accurate inputs, to generalized inputs. When presence less than 1% is predicted this implies that the plant group is only potentially present in insignificant amounts. Observed values below 1% should be regarded as not present. For a site with accurate data the predictions are accurate and quantitative. When generalized data are used, then the predictions show the correct order of magnitude and identifies the plant groups to be expected to be present. The sites Brattfors, Storulvsjön, Hensbacka and Vång lie in a straight line from north to south in Sweden, a distance 2,200 km long



5 Results

In Fig. 7 results have been assembled, the sites have been arranged according to their north-south orientation in Sweden. We have chosen four sites; starting from the north, Brattfors, next in middle Sweden, Storulvsjön, next one site in the southwestern part of Sweden, close to

Göteborg, Hensbacka and finally, one site in the south, Vång. The following color code has been adopted in all plots: Gray: Lichens and mosses, Blue: Heather and ling, Yellow: Grasses, Red: Brackens and ferns, Green: Herbaceous plants and flowers, Brown: Bushes, bush-like ling and thickets, the full legend is shown in Fig. 6. The model has been tested in several locations ranging

from northern to southern Sweden. These sites are among the Swedish forest integrated monitoring sites in the ICP-IM programme and are described in Martinson et al. 2005. The validation tests are shown in Fig. 8 where predicted for year 2001 has been plotted versus observed for year 2001. Validation of the ForSAFE-VEG model was done using data from the control plot at Svartberget, where the nitrogen addition experiments of (Strengbom et al. 2002) were conducted with good success. Validation of the ForSAFE model on forest production and soil chemistry has already been shown in Belyazid et al. (2005) among others (Aherne et al. 1998; Martinson et al. 2005; Sverdrup et al. 1995, 1996, 2005a; Sverdrup et al. 2005; Warfvinge et al. 1992, 1993). A comparison of measured against predicted growth, only calibrated on soil base saturation, has the fit of $\pm 1,6 \text{ kg m}^{-2}$ of biomass throughout the range from 5 to 24 kg m^{-2} of live biomass ($\pm 10\%$).

6 Discussion

The validation shows that with accurate data from a specific site, quantitative estimates of presence for each plant group can be achieved, and that all significant plants present are identified by the model. The fit with observed data is fair enough to say that the basic model works. When we switch to using more generalized input data and less site specific inputs, the model seems so far to produce the right order of magnitude of each plant group, and approximately identify the plant groups that can be expected to be present. The model frequently seems to miss with a large margin one or two plant groups, the reason for this has not yet been discovered. The runs have only been calibrated on initial base saturation at the start of a run, all other prediction follow from that, without any further model tuning. No other parameter, including the vegetation parameterization was adjusted in any way. Large vegetation changes occur at all sites in the period 1980–2010, so the degree of fit may appear worse than in reality as the timing of the prediction may be slightly off. Overall, the validation shows that the predictions are in the right order of magnitude and that the right kind of plant groups are

predicted to be present or not present. As we move from north to south, biodiversity increases and the response to change becomes stronger. The times when the sites went through clearing of the forests are evident. Towards modern times the responses in vegetation induced by change of any sort seems to become stronger. In the simulations, it becomes evident that when the system has been loaded up with nitrogen, changes in management or effects of pollution that change the internal fluxes inside the system, trigger larger effects than in the past.

A relevant question is to ask about the uncertainty of this kind of simulations. However, at this stage of research and model development, the question must be considered premature. What is seen here is the first stages in developing a new type of model, where we are in the middle of testing the model against observed data. The model presented here is a functional prototype, but the full spectrum of what the model will do is still under investigation. An important point is that the model is not calibrated to fit the data, this is done on purpose, the resulting misfits are very interesting diagnostic information for model development and necessary in order to adjust the parameterization, detect errors in the model and the different types of inputs. About the uncertainty of the simulations, we do not know at present, but work is ongoing to quantify it.

7 Conclusions

The tests on field data suggest that the basic structure of the VEG model integrated into the ForSAFE-VEG model cluster and its parameterization is in broad terms adequate and is capable of predicting a reasonable ground vegetation composition. The mechanistic formulation imply an *ab initio* prediction, suggesting that the included mechanisms are correctly expressed. The model performs well under conditions where the measurements are many and the chemical outputs can be verified. At the other sites, the history is obscure, but present vegetation is captured and significant changes as a response to air pollution, climate change and land use are predicted. We can conclude that a platform for developing a

tool for derivation of critical loads for nitrogen based on biodiversity has been achieved. Much work remain to be done on the model, and many questions concerning its limitations and potentials must still wait for some time.

Acknowledgements We would like in particular to give the following persons credit for cooperating with us in this endeavour: G. Halldorsson, B. Sigurdsson, A. Elmarsdottir, E. Oddsdottir, all at the Icelandic Forestry Institute at Mogilsá, S. R. Gislason at University of Iceland at the Geological Institute at the University of Iceland at Reykjavik and others involved in AFFORNORD, Trondur at Færöyane, P. Nygaard and O. Stubbestad at the Norwegian Agricultural University, Ås, L. Ericsson, J. Strengbom, A. Nordin, Umeå University. M. Svensson, P. Wallman, I. Stjernquist, G. Thelin, Lund University, Sweden. C. Beier, T. Mikkelsen, K. Pilegaard, I. Kappel Schmidt, P. Gundersen, S. Jonasson, at Copenhagen University and Risø National Laboratory. This research was supported by several integrated research programmes: AFFORNORD, a NordFa-project 2004–2008, ASTA, a MISTRA-programme Phase I+II 1999–2007, CLIMAITE, a VELUX-programme 2004–2008, SUFOR, a MISTRA-programme Phase I+II 1996–2004.

References

- Aber, J. D., Ollinger, S. V., Federer, C., Reich, P. B., Gould, M. L., Kirklighter, D. W., et al. (1995). Predicting the effects of climate change on water yield and forest production in the Northeastern United States. *Climate Research*, 5, 207–222.
- Aherne, J., Sverdrup, H., Farrell, E., & Cummins, T. (1998). Application of the SAFE model to a Norway spruce stand at Ballyhooly, Ireland. *Forest Ecology and Management*, 101, 331–338.
- Akselsson C., Ardö J., & Sverdrup, H. (2004). Critical loads of acidity for forest soils and relationship to forest decline in the northern Czech Republic. *Environmental Monitoring and Assessment*, 98, 363–379.
- Alveteg, M., Sverdrup, H., & Warfvinge, P. P. (1996). Regional assessment of dynamic aspects of soil acidification in southern Sweden. *Water, Air and Soil Pollution*, 85, 2509–2514.
- Alveteg, M., Walse, C., & Sverdrup, H. (1998). Evaluating simplifications used in regional applications of SAFE and MAKEDEP models. *Ecological Modelling*, 107, 265–277.
- Barkman, A., Warfvinge, P., & Sverdrup, H. (1996). Regionalization of critical loads under uncertainty. *Water, Air and Soil Pollution*, 85, 2515–2520.
- Barkman, A., Schlyter, P., Lejonklev, M., Alveteg M., Warfvinge, P., Sverdrup, H., et al. (1999). Uncertainties in high resolution critical load assessment for forest soils – possibilities and constraints of combining distributed soil modelling and GIS. *Environmental and Geographical Modeling*, 3(2), 125–143.
- Belyazid, S., Sverdrup, H., & Alveteg, M. (2005). The biogeochemical models family of the biogeochemistry group at Lund University. In *Proceedings from a UN/ECE conference held in Pushino, Russia September 16–18, 2004. Institute of Soils Science and Phytobiology, Nauka, September 2004*. (Also printed in Belyazid, S.: Dynamic modelling of biogeochemical processes in forest ecosystems. PhD Thesis from Chemical Engineering, Lund University, Box 124, 22100 Lund, Sweden. *Reports in ecology and environmental engineering*, 2006 (1), 46–58).
- Belyazid, S., Westling, O., & Sverdrup, H. (2006). Modelling changes in soil chemistry at 16 Swedish coniferous forest sites following deposition reduction. *Environmental Pollution* (in press).
- Berghthorsson, P. (1985). Sensitivity of Icelandic agriculture to climatic variations. *Climatic Change*, 7, 111–127.
- Bobbink, R., Ashmore, M., Braun, S., Flueckiger, W., & van den Wyngaert, I. I. J. (2002). Empirical critical loads for natural and semi-natural ecosystems: 2002 update. In R. Bobbink (Ed.), *Empirical critical loads for nitrogen* (pp.43–170). Bern, Schweiz: Swiss Agency for Environment, Forests and Landscape.
- EEA (1996). *The Dobbris assessment*. Copenhagen: European Environmental Agency (EEA). <http://www.biodiversity.be/bbpf/econf/econfdath.html>
- Ellenberg, H. (1992). Zeigerwerte von Pflanzen in mitteleuropa. *Scripta Geobotanica*, 18.
- European Commission (1995). Brussels: Europeans and the environment.
- Falkengren-Grerup, U. (1992). Mark och floraförändringar i sydsvensk adellövskog. Naturvårdverket Rapport 4061.
- Fridriksson, S., & Sigurdsson, F. H. (1983). Áhrif lofthita á grassprettu. *J. Agr. Res. Icelandica*, 15, 41–54.
- Green, D. G., & Klomp, N. I. (1996). Ecosystem connectivity and its implications for managing biodiversity. In R. Crozier & S. Lawler (Eds.), *Setting conservation priorities*. Cambridge, UK: Cambridge University Press.
- Grennfelt, P., & Hov, Ø. (2005). Regional air pollution at a turning point. *Ambio*, 34, 2–10.
- Grennfelt, P., Moldan, F., Alveteg, M., Warfvinge, P., & Sverdrup, H. (2001). Critical loads – is there a need for a new concept. *Journal of Water, Air and Soil Pollution Focus* 1, 21–27.
- Guyot, G. (1998). *Physics of the environment and climate*. Paris: Wiley.
- Hanks, J., & Ritchie, J. (1991). Modelling plant and soil systems. In *Agronomy* 3. New York: Soil Science Society of America.
- Hansson, J. (1995). Experimenting with modeling of biodiversity as a function of soil acidity and nitrogen. *Report in Ecology and Environmental Engineering* 3. Lund, Sweden: Chemical Engineering II, University of Lund.
- Kimmins, H. (1996). *Forest Ecology. A foundation for sustainable management* (2nd ed., 6 pp. Edition ISBN 0-02-364071-5). New Jersey: Prentice Hall.

- Lambers, H., Stuart Chapin, E., & Pons, T. (1998). *Plant physiological ecology*. Berlin Heidelberg New York: Springer.
- Larcher, W. (1975–1995). *Physiological plant ecology*. Berlin Heidelberg New York: Springer.
- Latour, J. B., Reiling, R., & Slooff, W. (1994). Ecological limit values for eutrophication and desiccation: perspectives for a risk assessment. *Water Air and Soil Pollution*, 78, 265–277.
- Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends. 251 pp. *UNECE Convention on Long-range Transboundary Air Pollution (LRTAP)*, Geneva. Mapping Manual 2004, www.icpmapping.org.
- Marschner, H. (1991). Mechanisms of adaption of plants to acid soils. *Plant and Soil*, 134, 1–20.
- Marschner, H. (1997). *Mineral nutrients of higher plants*. London: Academic.
- Martinson, L., Alveteg, M., Kronnas, V., Sverdrup, H., Westling O., & Warfvinge, P. (2005). A regional perspective on present and future soil chemistry at 16 Swedish forest sites. *Water, Air and Soil Pollution*, 4, 1–20.
- Mossberg, B., & Stenberg, L. (1997). Den Nordiska Floran. Stockholm: Wahlström & Widstrand Forlag. ISBN 9146175849.
- Nilsson, S. G., Niklasson, M., Hedin, J., Eliasson, P., Ljungberg, H. (2005). Biodiversity and sustainable forestry in changing landscape – principles and Southern Sweden as an example. *Journal of Sustainable Forestry*, 21, 11–43.
- Nordin, A., Strengbom, J., Witzell, J., Näsholm, T., Ericson, L. (2004). Nitrogen deposition and the biodiversity of boreal forests: Implications for the nitrogen critical load. *Ambio*, 34, 20–24.
- Stjernquist, I., Rosengren, U., Sonesson, K., Sverdrup, H., Thelin, G., & Nihlgård, B. (2002a). Forest health indicators. In H. Sverdrup & I. Stjernquist (Eds.), *Developing principles for sustainable forestry. Results from a research program in southern Sweden. Managing forest ecosystems* (vol. 5, pp. 204–213). Amsterdam: Kluwer.
- Stjernquist, I., Sverdrup, H., & Welander, T. (2002b). Acid deposition and soil acidity. In H. Sverdrup & I. Stjernquist (Eds.), *Developing principles for sustainable forestry. Results from a research program in southern Sweden. Managing forest ecosystems* (vol. 5, pp. 222–236). Amsterdam: Kluwer.
- Strengbom, J., Nordin, A., Näsholm, T., & Ericson, L. (2002). Parasitic fungus mediates vegetational changes in nitrogen-exposed boreal forests. *Journal of Ecology* 90, 61–67.
- Svensson, M. G. E., Stjernquist, I., Schlyter, P., & Sverdrup, H. (2002). Biodiversity in sustainable forestry. In H. Sverdrup & I. Stjernquist (Eds.), *Developing principles for sustainable forestry Results from a research program in southern Sweden. Managing forest ecosystems* (vol. 5, pp. 273–283). Amsterdam: Kluwer.
- Sverdrup, H., & Warfvinge, P. (1993a). The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. In *Reports in Ecology and Environmental Engineering 2:1993*. Lund Sweden: Chemical Engineering II, University of Lund, Lund, Sweden.
- Sverdrup, H., & Warfvinge, P. (1993b). Calculating field weathering rates using a mechanistic geochemical model PROFILE. *Applied Geochemistry*, 8, 273–283.
- Sverdrup, H., Warfvinge, P., Blake, L., & Goulding, K. (1995). Modelling recent and historic soil data from the Rothamsted experimental station, UK, using SAFE. *Agriculture, Ecosystems and Environment*, 53, 161–177.
- Sverdrup, H., Hagen-Thorn, A., Holmqvist, J., Warfvinge, P., Walse, C., & Alveteg, C. (2002). Biogeochemical processes and mechanisms. In H. Sverdrup, & I. Stjernquist, (Eds.), *Developing principles for sustainable forestry. Results from a research program in southern Sweden. Managing forest ecosystems* (vol. 5, pp. 91–196). Amsterdam: Kluwer.
- Sverdrup, H., Martinsson, L., Alveteg, M., Moldan, F., Kronnas, V., & Munthe, J. (2005). Modeling recovery of Swedish ecosystems from acidification. *Ambio*, 34, 25–31.
- Sverdrup, H., Belyazid, S., Haraldsson, H., Nihlgård, B. (2005). Modelling change in ground vegetation from effects of nutrients, pollution, climate, grazing and land use. In Edda & Gudmundur Halldorsson (Eds.), *Effects of afforestation on ecosystems, landscape and rural development. Proceedings from a conference held at Reykholt June 20–23, 2005. Andre nordiske publikasjoner*, Chapter 2:14–21. Copenhagen: Nordic Council of Ministers.
- Sverdrup, H., Warfvinge, P., Moldan, F., & Hultberg, H. (1996). Modelling acidification and recovery in the roofed catchment at lake Gårdsjön, using the SAFE model. *Water, Air and Soil Pollution*, 85, 1753–1758.
- Tilman, D. (1994). Competition and biodiversity in spatially structured habitats. *Ecology*, 72, 2–16.
- Ulrich, B. (1985). Interaction of indirect and direct effects of air pollutants in forests. In C. Tryanowsky (Ed.), *Air pollution and plants* (pp. 149–181). Weinheim: Gesellschaft Deutsche Chemiker VCH Verlagsgesellschaft.
- Wallman, P., Sverdrup, H., Svensson, M., & Alveteg, M. (2002). Integrated modelling. In H. Sverdrup & I. Stjernquist (Eds.), *Developing principles for sustainable forestry. Results from a research program in southern Sweden. Managing Forest Ecosystems* (vol. 5, pp. 57–83). Amsterdam: Kluwer.
- Walse, C. (1998). Modelling acidification and nutrient supply in forest soil. Report in Ecology and Environmental Engineering 2. PhD thesis. Sweden: Chemical Engineering II, University of Lund.
- Warfvinge, P., Sverdrup, H., Ågren, G., & Rosen, K. (1992). Effekter av luftföroreningar på framtida skogstillväxt. In *Skogspolitiken inför 2000 talet – 1990 års skogspolitiska kommitté, Statens Offentliga Utredningar: SOU* (vol. 76, pp. 377–412).
- Warfvinge P., Falkengren-Grerup, U., Sverdrup, H., & Andersen, B. (1993). Modelling long-term cation supply in acidified forest stands. *Environmental*, 80, 209–221.

Laboratory Measurement of Dry Deposition of Ozone onto Northern Chinese Soil Samples

Atsuyuki Sorimachi · Kazuhiko Sakamoto

Published online: 23 March 2007
© Springer Science + Business Media B.V. 2007

Abstract We used laboratory experiments to investigate surface resistance (R_c) to dry deposition of ozone (O_3) on different types of soil samples collected from the arid deserts and the Loess Plateau of northern China. Furthermore, we measured the factors that affected R_c , which depends on the physical and chemical interaction between trace constituents and the deposition surface, and evaluated deposition velocity (V_d). There was little influence of geometric surface area, soil weight, or O_3 concentration on V_d of O_3 . The effect of relative humidity (RH) (i.e. moisture content of the soil) on O_3 uptake was in agreement with results reported in the literature: a distinct RH dependence of V_d and little uptake under water-saturated conditions were observed. R_c values for all the soil samples examined were in the range 0.21–3.3 s mm⁻¹ and were exponentially related to the surface area of the particles and the organic carbon content of each soil sample at RH of both <10 and 60%.

Keywords China · Deposition velocity · Ozone · Relative humidity · Soil surface resistance

1 Introduction

In northern China there are vast arid areas such as the Loess Plateau and the Gobi Desert. Because the airborne particles derived from such areas are alkaline, they play an important role in the buffering and neutralizing of acidic substances (Wang and Wang 1996; Zhao et al. 1988). Examination of the extent of uptake of acidic gases over such areas may provide interesting information about the transport and fate of these gases. However, in East Asia few direct dry deposition measurements have been made, although many such measurements have been taken in North America and Europe (Erisman et al. 1994; Voldner et al. 1986; Wesely and Hicks 2000).

So far, we have measured dry deposition fluxes of SO_2 in northern China during short periods (Sorimachi et al. 2003, 2004; Utiyama et al. 2005). Because of the increase in atmospheric O_3 concentration, mainly as a result of higher rates of NO_x emission from industry and combustion of fossil fuel by automobiles, we have also measured O_3 dry deposition fluxes simultaneously with SO_2 (Sorimachi et al. 2003). However, the vast areas and variable soil compositions make direct dry deposition measurements difficult. Furthermore, if micrometeorological methods were to be employed, they would entail huge expenditures of money, time, and effort.

Therefore, under constant environmental conditions in the laboratory, we measured soil surface resistance (R_c) to dry deposition of O_3 in different types of samples collected in northern China, and we

A. Sorimachi · K. Sakamoto (✉)
Department of Environmental Science and Human
Engineering, Graduate School of Science and Engineering,
Saitama University,
255 Shimo-ohkubo, Sakura-ku,
Saitama City, Saitama 338-8570, Japan
e-mail: sakakazu@env.gse.saitama-u.ac.jp

analyzed the factors that affected R_c . We chose to do these experiments in the laboratory because the use of field measurements would not have allowed us to easily separate soil parameters from other parameters.

2 Experimental Method

Laboratory measurement of O_3 dry deposition was carried using native soils collected from 12 sites (Fig. 1). Native soil was collected from the ground surface (depth 0 mm) to about 100 mm at each site. After the removal of plants, roots, and large particles, the resulting material was dried at 105°C for at least 4 h in an electric oven.

The procedure used to prepare the deposition surface and the schematic diagram of the acrylic cylindrical reactor (112 mm i.d. $\times$ 138 mm height) used have been published elsewhere in detail (Sorimachi et al. 2004). The soil surface, which was prepared by evenly distributing a known weight of the soil sample on a polyethylene sample plate (21.2 mm i.d. $\times$ 1 mm height, surface area 353 mm^2), was placed in the reactor before the exposure experiment was begun.

Ozone was produced by UV radiation to purified air in a mixing chamber before introduction into the reactor, and the concentrations at the inlet and outlet of the reactor were monitored continuously by a UVAD-1000 UV absorption O_3 monitor (Shimadzu Co. Ltd., Kyoto). During the experiment, the reactor was covered with a blackout curtain to shut out extraneous light at room temperature ($25 \pm 1^\circ\text{C}$).

Deposition velocity, V_d , at a reference height, z , was defined by the usual expression relating dry

deposition flux, F , to concentration, C , assuming zero surface concentration (Erisman et al. 1994; Wesely and Hicks 2000):

$$F = V_d(z)C(z) \quad (1)$$

V_d provides a measure of the conductivity of the atmosphere-surface combination for the gas and is used widely to parameterize gas uptake at the ground surface. The reciprocal of V_d is resistance to deposition, which is usually divided into three terms:

$$V_d(z) = (R_a + R_b + R_c)^{-1} \quad (2)$$

The three resistances represent the three stages of transport: R_a is the aerodynamic resistance; R_b is the quasi-laminar boundary layer resistance; and R_c is the surface or canopy resistance, which depends on the physical and chemical interaction between the trace constituents and the deposition surface.

F was estimated from the following equation:

$$F = (A - B)/(S_{\text{GEO}}t) \quad (3)$$

where A and B are the amounts of O_3 deposition with and without the soil sample in the reactor, respectively, and are estimated from the integrated difference between the concentrations at the inlet and outlet, as measured by the monitor ($g\text{-O}_3$), S_{GEO} is the geometric surface area of the soil plate covered by soil exposed to the experimental gas (m^2), and t is the duration of exposure to the experimental gas (s). In calculating V_d by Eq. 1, C was assumed to be the concentration of the experimental gas at the reactor inlet.

Soil samples were characterized by their Brunauer–Emmett–Teller surface area (S_{BET}), using a Micromeritics Flowsorb III 2305 nitrogen adsorption apparatus, and by their acidity, which was evaluated with a glass electrode (Metrohm, Herisau, Switzerland) as the pH of a mixture prepared by putting 1 mg treated soil into 1 ml ultrapure water. S_{BET} and pH (H_2O) values are listed in Table 1.

Organic carbon (OC) content was determined from the difference between total carbon (TC) and carbonate carbon (CO_3^{2-}). TC content was quantified by a Yanaco MT-3 CHN Corder, and CO_3^{2-} content was determined by a Fuji Electric ZALDBZ 511–10 non-dispersive infrared gas analyzer for CO_2 gas, which was produced by the reaction between CO_3^{2-} and phosphoric acid solution (Wang and Sakamoto 1994). Also, calcium (Ca^{2+}) was subjected ultrasonic extraction with known volumes of ultrapure water and the

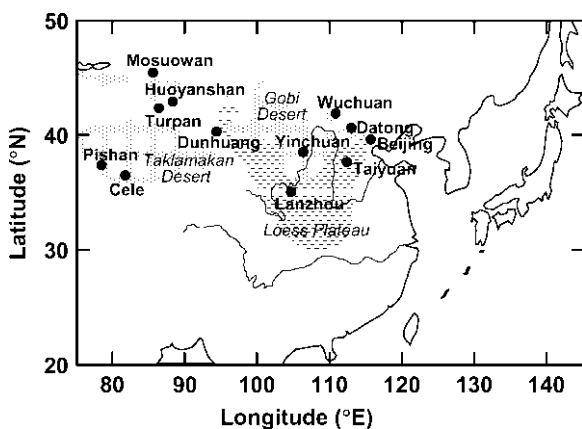


Fig. 1 Map of soil collection sites in northern China

extracts were filtered and then assayed by ion chromatography. Much of the soil in northern China contains more than 3% Ca, which is a prominent alkaline component of soil (Dong et al. 1999). Table 1 shows that the Ca^{2+} content of most of the soil samples was more than 3%, which was similar to the finding reported by Dong et al. (1999). Also the Ca^{2+} in our soil samples presented as CaCO_3 by the fact that least-squares regression between the concentrations of Ca^{2+} and CO_3^{2-} in molar units revealed a line slope of 0.99, with an intercept set to zero ($r=0.84$, $p<0.01$, $n=12$).

3 Results and Discussion

3.1 Aerodynamic Characteristics of the Reactor

In the initial experiments, the relationship between linear velocity (u) and R_a+R_b in the reactor was determined for $u=0.89\text{--}6.8\text{ mm s}^{-1}$ (corresponding to flow rate, $f,=0.53\text{--}4.0\text{ l min}^{-1}$). For this purpose, charcoal was used as the deposition surface by laying it on the plate in place of the soil sample. The charcoal was obtained from granular charcoal (Wako Pure Chemical Industries, Ltd., Osaka), which was ground in an agate mortar to yield powders and was sieved with 100 mesh to remove particles less than

125 μm in diameter. The resulting material was dried in the same way as the soil samples. Assuming that the R_c for charcoal was approximately zero (i.e., a perfectly depositing surface) (Galbally and Roy 1980), the V_d of O_3 onto charcoal was inversely proportional to R_a+R_b , from Eq. 2:

$$V_d \cong (R_a + R_b)^{-1} \quad (4)$$

In blank experiments conducted without the soil samples, we tested adsorption of O_3 on the wall of the reactor. We observed a systematic temporal pattern in which the rate of uptake was initially high and gradually decreased (not shown). Using 150 mg charcoal for $1,059\text{-mm}^2 S_{\text{GEO}}$ at $<10\%$ RH, an initially high rate was observed, as in the case with the blank; the O_3 concentration at the outlet initially decreased rapidly to about 20% of that at the inlet, increased exponentially within the first 2 h, and then remained almost constant at about 70% of that at the inlet (not shown). Taking into account this uptake of O_3 on the wall, the concentration at the outlet after passing over the charcoal surface remained constant during the exposure period; the amount of O_3 deposited was in proportion to the exposure amount, and thus the exposure time. Consequently, we concluded that little buildup of corrosion products on the charcoal surfaces occurred.

Table 1 Characteristics of Chinese soil samples used

Soil	pH (H_2O)	Ca^{2+} [%]	OC [%] ^a	CO_3^{2-} [%] ^a	S_{BET} [m^2 (g-soil) ⁻¹]	Soil wt. ^b [mg]
Beijing	9.8	2.9	1.0	0.74	10	300
Datong	9.8	3.8	0.6	0.91	10	300
Taiyuan	9.9	4.6	0.3	1.4	12	300
Wuchuan	7.6	0.34	0.72	n.d. ^d	1.4	900
Yinchuan	9.6	4.0	0.3	1.2	7.6	300
Lanzhou	9.7	4.2	1.6	1.6	9.4	150
Dunhuang	8.9	4.9	0 ^c	1.6	0.37	600
Huoyanshan	9.4	6.2	0.1	1.1	10	300
Turpan	9.7	2.8	0.3	0.79	2.9	300
Mosuwon	9.8	2.9	0.19	0.80	17	300
Cele	9.6	6.0	0.1	1.9	1.8	150
Pishan	9.5	6.2	0 ^c	1.9	0.76	300

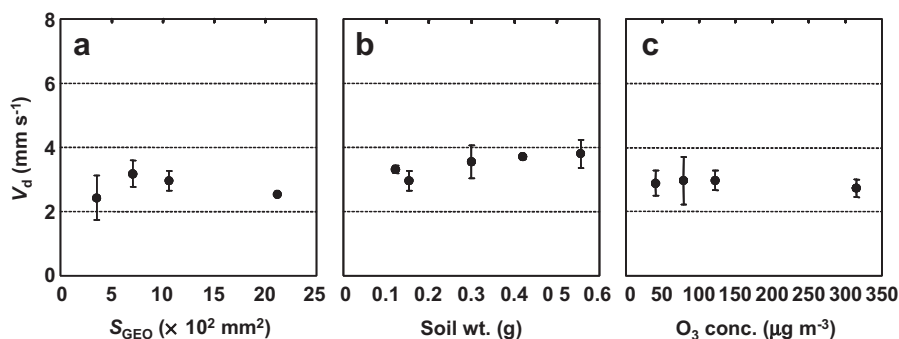
^a [$\text{g-C (g-soil)}^{-1} \times 100$].

^b Approximate sample weight of the soils studied.

^c Negative values were obtained.

^d Not detected (less than 0.03%).

Fig. 2 Effects of V_d of O_3 on Lanzhou soil surfaces on (a) geometric surface area (S_{GEO}), (b) soil weight, and (c) O_3 concentration. Bars represent standard deviations ($n=3$ or 4)



As in the experiment of Sorimachi et al. (2004) for SO_2 , mass transfer through a turbulent boundary layer depends on wind speed. The expression:

$$V_d \cong 4.2u^{0.49} \quad (5)$$

with V_d and u in mm s⁻¹, was presented ($r=0.94$, $p<0.02$, $n=5$), whereas the corresponding expression for $R_a + R_b$ was as follows ($r=0.94$, $p<0.02$, $n=5$):

$$R_a + R_b \cong 0.24u^{-0.48} \quad (6)$$

This relationship can be used to estimate R_c for soil samples exposed under similar aerodynamic conditions in the reactor. If R_c is zero, which implies a perfect sink, then $R_a + R_b$ is the rate-limiting resistance, and V_d takes a maximum value. V_d ranged from 3.6 to 10 mm s⁻¹, corresponding to $u=0.89$ – 6.8 mm s⁻¹. At 60% RH, V_d at f of 3.1 l min⁻¹ was 10 (± 3.5) mm s⁻¹ and differed little from the value at <10% RH.

3.2 Influence of Soil Parameters on Uptake of O_3

The Lanzhou soil sample was exposed to O_3 for 3 h at a 3-l min⁻¹ flow rate in order to investigate factors such as S_{GEO} , soil weight, O_3 concentration, and RH. Among such experiments, a systematic temporal pattern similar to that of the charcoal was obtained (not shown).

Figure 2a shows the relationship between V_d and S_{GEO} ranging from 353 to 2,118 mm² (the corresponding soil weight ranged from 50 to 300 mg) at 120- μ g m⁻³ O_3 concentration and <10% RH. Here the measurements were made by changing the number of sample plate that S_{GEO} was 353 mm² for 50-mg soil sample. The observed mean V_d value was 2.8 mm s⁻¹, and there was little variation in V_d of O_3 with changes in S_{GEO} .

The effect of soil weight on V_d is presented in Fig. 2b at 120- μ g m⁻³ O_3 concentration and <10% RH. Here the measurements were made by keeping the S_{GEO} at 1,059-mm² and by changing the weight of soil put on each of three sample plates. Little variation in V_d occurred with changes in soil weight, as was the case for S_{GEO} .

Figure 2c shows the effect of O_3 concentration, ranging from 40 to 320 μ g m⁻³, on V_d at 1,059-mm² S_{GEO} for 150-mg soil samples and <10% RH. Little variation in V_d was observed with O_3 concentration, as was the case with S_{GEO} , indicating that

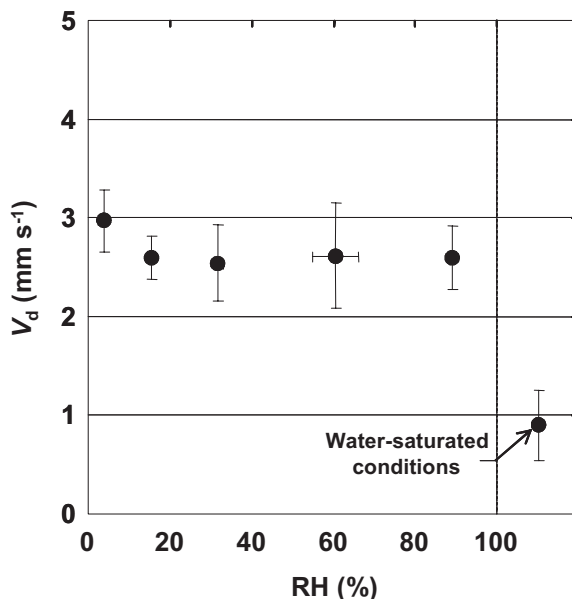


Fig. 3 Relationship between V_d of O_3 and RH. The Lanzhou soil samples were exposed for 3 h at 3-L min⁻¹ flow rate, 120- μ g m⁻³ O_3 concentration, and 25°C. The geometric surface area was 1059 mm² for 150-mg soil samples. Bars represent standard deviation ($n=3$ or 4)

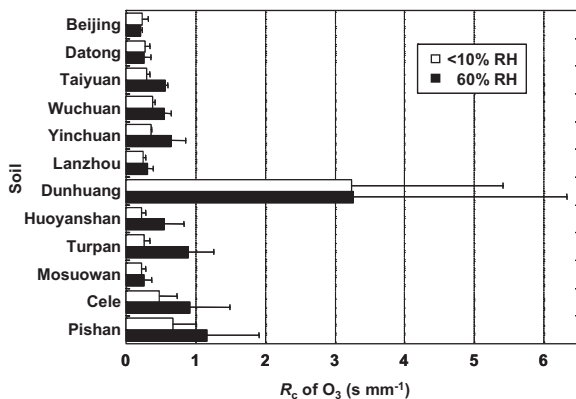


Fig. 4 R_c to O_3 deposition. Soil samples were exposed for 3 h at 3-L min^{-1} flow rate, $120\text{-}\mu\text{g m}^{-3}$ O_3 concentration, and 25°C . Fine bars represent standard deviation ($n=3$ or 4)

there was insignificant buildup of corrosion products on the soil surface.

Figure 3 shows the relationship between V_d and RH at $120\text{-}\mu\text{g m}^{-3}$ O_3 concentration and $1,059\text{-mm}^2 S_{\text{GEO}}$ for 150-mg soil samples. Within the range of RH 0–30%, the values of V_d decreased by 14% with an increase in RH, whereas at RH more than 30% little variation in V_d was observed. It is generally believed that wet bare soil has a larger surface resistance to ozone uptake than dry bare soil (Erisman et al. 1994; Wesely and Hicks 2000). Therefore, increasing the moisture content of the soil, which decreases soil porosity and reduces the surface area available to the O_3 , increases the soil's resistance to O_3 removal. Furthermore, at water-saturated soil conditions (soil/water=1 mg/10 mg), the V_d value was 0.90 mm s^{-1} (Fig. 3), whereas the corresponding

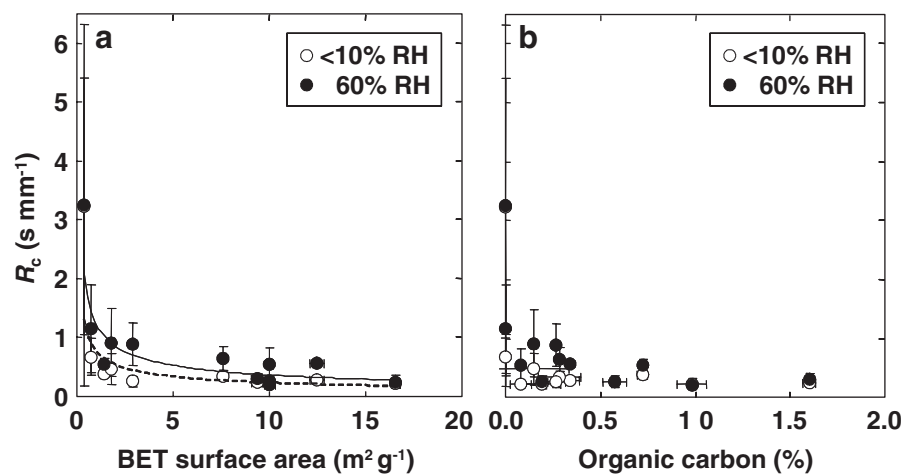
R_c value was 1.3 s mm^{-1} , which was consistent with the value of Wesely et al. (1981) of 1 s mm^{-1} for cold bare soil well saturated with water.

3.3 Surface Resistance of Northern Chinese Soils to O_3 Deposition

Similarly to the Lanzhou soil, the other Chinese soil samples were exposed to O_3 over 3 h at 3-L min^{-1} flow rate and $1,059\text{-mm}^2 S_{\text{GEO}}$, with soil weights ranging from 150 to 900 mg (Table 1). The systematic temporal patterns found were similar to those of the charcoal and the Lanzhou soil (not show). The mean values of R_c for the Chinese soil samples, excluding the Dunhuang soil sample (Fig. 4), were $0.33\pm0.13\text{ s mm}^{-1}$ at <10% RH and $0.57\pm0.30\text{ s mm}^{-1}$ at 60% RH. Our findings seemed to be the same tendency as those in a review by Massman (2004), which indicated R_c for dry soil in the range $0.01\text{--}0.18\text{ s mm}^{-1}$ and for wet soil in the range $0.18\text{--}1.1\text{ s mm}^{-1}$. The value of R_c for Dunhuang was significantly larger than the others, indicating that the dry deposition potential of O_3 over the Dunhuang region was smaller than over the others. Thus a low removal rate of O_3 may have a marked influence on the ecosystem, air-surface exchange, and transport processes.

Figure 4 indicates a wide range in the values of R_c for the northern Chinese soil samples. The uptake of O_3 by most of the soil samples seemed to be dependent on RH, as noted in the preceding section. R_c was comparable to, or larger than, $R_a + R_b$ and had a marked influence on V_d . Therefore, the variation in R_c (and V_d) for each soil sample may be dependent on the

Fig. 5 Relationship between R_c of O_3 and (a) S_{BET} and (b) organic carbon. Data on R_c in this figure are the same as those used in Fig. 4. Dashed and solid lines are best fits to data at <10% RH and 60% RH, respectively. Bars represent standard deviation ($n=3$ or 4)



soil characteristics of soil porosity, soil moisture, and soil organic content (Massman 2004), under our conditions of atmospheric transfer ($R_a + R_b$), which were similar for each soil sample.

Figure 5 shows the relationship between R_c and S_{BET} . R_c values decreased exponentially with increasing S_{BET} ($r=0.85$, $p<0.01$, $n=12$, $RH <10$ or 60%). Furthermore, similarly to S_{BET} , R_c seemed to be related exponentially to OC content at both $<10\%$ RH and 60% RH. This suggests that physical and/or chemical differences in the soil particles affect the uptake of O_3 by the soil.

4 Conclusions

In the laboratory we measured O_3 dry deposition onto the surfaces of northern Chinese soils. We obtained the following results:

1. Factors such as geometric surface area, soil weight, or O_3 concentration had little influence on the uptake of O_3 .
2. Relative humidity was related to uptake of O_3 by the soil surface; in particular, a distinct decrease in uptake in the range 0–30% RH was observed. Uptake of O_3 under water-saturated conditions was about three times smaller than that at $<10\%$ RH.
3. Assuming that the charcoal was a perfect deposition surface, the values of R_c for northern Chinese soil samples ranged from 0.21 to 3.3 s mm^{-1} and were exponentially related to the surface area of the particles and organic carbon content of each soil sample.

Acknowledgments This work was supported by a Grant-in-Aid for Scientific Research (KAKENHI) [No. 15254001 (2003–2005)] from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We wish to thank the Chinese Research Academy of Environmental Sciences and the Sino-Japanese Friendship Center for Environmental Protection for supporting this work.

References

- Dong, X., Sakamoto, K., Zheng, C., Quan, H., Chen, Y., & Wang, W. (1999). Characteristics of Ca and Mg distribution in soil of China and their relationship to acidic pollutants in the atmosphere. *J. Aerosol Res., Jpn.*, 14, 171–180 (in Japanese with English abstract).
- Erisman, J. W., van Pul, A., & Wyers, P. (1994). Parametrization of surface resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone. *Atmospheric Environment*, 28, 2595–2607.
- Galbally, I. E., & Roy, C. R. (1980). Destruction of ozone at the earth's surface. *Quarterly Journal of the Royal Meteorological Society*, 106, 599–620.
- Massman, W. J. (2004). Toward an ozone standard to protect vegetation based on effective dose: A review of deposition resistances and a possible metric. *Atmospheric Environment*, 38, 2323–2337.
- Sorimachi, A., Sakamoto, K., Ishihara, H., Fukuyama, T., Utiyama, M., Liu, H., et al. (2003). Measurements of sulfur dioxide and ozone dry deposition over short vegetation in northern China – a preliminary study. *Atmospheric Environment*, 37, 3157–3166.
- Sorimachi, A., Sakamoto, K., Sakai, M., Ishihara, H., Fukuyama, T., Utiyama, M., et al. (2004). Laboratory and field measurements of dry deposition of sulfur dioxide onto Chinese loess surfaces. *Environmental Science and Technology*, 38, 3396–3404.
- Utiyama, M., Fukuyama, T., Sakamoto, K., Ishihara, H., Sorimachi, A., Tanonaka, T., et al. (2005). Sulfur dioxide dry deposition on the loess surface – surface reaction concept for measuring dry deposition flux. *Atmospheric Environment*, 39, 329–335.
- Voldner, E. C., Barrie, L. A., & Sirois, A. (1986). A literature review of dry deposition of oxides of sulphur and nitrogen with emphasis on long-range transport modelling in North America. *Atmospheric Environment*, 20, 2101–2123.
- Wang, Q. Y., & Sakamoto, K. (1994). Spatial difference of carbonate components in soil and road dust and their relationship with ambient aerosol acidity. *J. Aerosol Res. Jpn.*, 9, 345–353 (in Japanese with English abstract).
- Wang, W., & Wang, T. (1996). On acid rain formation in China. *Atmospheric Environment*, 30, 4091–4093.
- Wesely, M. L., Cook, D. R., & Williams, R. M. (1981). Field measurement of small ozone fluxes to snow, wet bare soil, and lake water. *Boundary-Layer Meteorol.*, 20, 459–471.
- Wesely, M. L., & Hicks, B. B. (2000). A review of the current status of knowledge on dry deposition. *Atmospheric Environment*, 34, 2261–2282.
- Zhao, D., Xiong, J., Xu, Y., & Chan, W. H. (1988). Acid rain in southwestern China. *Atmospheric Environment*, 22, 349–358.

Ozone Deposition to a Coniferous and Deciduous Forest in the Czech Republic

Miloš Zapletal · Petr Chroust

Published online: 5 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Estimates of ozone concentration and deposition flux to coniferous and deciduous forest in the Czech Republic on a 1×1 km grid during growing season (April–September) of the year 2001 are presented. Ozone deposition flux was derived from ozone concentrations in the atmosphere and from its deposition velocities. To quantify the spatial pattern in surface concentrations at 1 km resolution incorporating topography, empirical methods are used. The procedure maps ozone concentrations from the period of the day when measurements are representative for the forest areas of countryside. The effects of boundary layer stability are quantified using the observed relationship between the diurnal variability of surface ozone concentration and altitude. Ozone deposition velocities were calculated according to a multiple resistance model incorporating aerodynamic resistance (R_a), laminar layer resistance (R_b) and surface resistance (R_c). Surface resistance (R_c) comprises stomatal resistance (R_{sto}). R_{sto} was calculated with respect to global radiation, surface air temperature and land cover. Modelled total and stomatal ozone fluxes are compared with the maps describing equivalent values of AOT40 (accumulated exposure over threshold of 40 ppb). For forests, the critical level (9,000 ppbh May–July

daylight hours) is exceeded over 50% of forested territory. This indicates the potential for effects on large areas of forest. There is significant correspondence between the exposure index AOT40 and the total ozone flux, but the relation between the total ozone flux and AOT40 exposure index is not clear in all parts of the forest territory.

Keywords AOT40 · mapping · ozone concentration · ozone deposition · resistance model · stomatal fluxes · topographic effects · tropospheric ozone

1 Introduction

Ozone is one of the most important phytotoxic air pollutant affecting forest trees in large areas of Europe. There is evidence that the ambient ozone concentrations found in Europe can cause a range of effects to vegetation, including visible leaf injury, growth and yield reduction, and altered sensitivity to biotic and additional abiotic stresses (Ashmore, Emberson, Karlsson, & Pleijel, 2004; Karlsson, Selldén, & Pleijel, 2003; UNECE, 2005).

In 1988, the United Nations Economic Commission for Europe (UN-ECE) adopted the critical levels concept. The critical levels were defined as “the concentrations of pollutants above which direct adverse effects on receptor, such as plant, ecosystems or materials, may occur according to the current knowledge” (UNECE, 1988).

M. Zapletal (✉) · P. Chroust
Centre for Environment and Land Assessment – Ekotoxa
Opava, Horní nám. 2, 746 01 Opava, Czech Republic
e-mail: milos.zapletal@ekotoxa.cz

Level I ozone critical levels for forest trees were based upon the AOT40 concept (Fuhrer & Acherman, 1994; Kärenlampi & Skärby, 1996) and defined as cumulative exposure over a threshold concentration of 40 ppb over a set up time period. The description and critical assessment of scientific basis for the critical levels for ozone AOT40 and identification of its advantages and uncertainties are given by Fuhrer, Skärby, and Ashmore (1997). The AOT40 corresponds to ozone exposure associated with significant negative effects on the biomass increment of forest trees (Fuhrer et al., 1997).

However, level I approach has a number of serious problems if the aim is to assess likely ozone damage to vegetation. AOT40 is calculated only on the basis of ambient ozone concentrations regardless of whether this ozone is actually absorbed by the plant or not (Emberson, Simpson, Tuovinen, Ashmore, & Cambridge, 2000a; Emberson, Ashmore, Cambridge, Simpson, & Tuovinen, 2000b; Emberson, Wieser, & Ashmore, 2000c; Emberson, Ashmore, Simpson, Tuovinen, & Cambridge, 2001). The development of a physiologically based cause–effects relationship for ozone requires that the ozone exposure should be described as leaf cumulative uptake of ozone (CUO), based on ozone flux estimates (Fuhrer, 2000).

At the CLRTAP workshop in Gothenburg, 2002 (Bull, Karlsson, Sellden, & Pleijel, 2003), two alternative approaches were considered, based on modeled stomatal ozone flux and on the maximum permissible ozone concentration (MPOC). Ashmore et al. (2004); Ashmore, Emberson, Karlsson, & Pleijel, 2005) and Krause et al. (2005a, b) present an assessment of the strengths and weaknesses of these approaches from the scientific perspective, as well as from a perspective of continental-scale regional risk assessment and policy evaluation.

Matyssek et al. (2004) demonstrated that in both seedlings and adult trees AOT40 may show some linearity in correlations with average cumulative O_3 uptake. Field studies from Bavaria with mature trees provide evidence that stomatal flux is a better predictor of injury than is AOT40 (Ashmore et al., 2004).

Karlsson et al. (2004) derive ozone uptake – biomass response relationship for young trees from existing experiments for a number of deciduous and conifer species, to compare these relationships with those based on daylight AOTx and to use the

relationships to suggest new ozone critical levels for trees, at Level I and cumulated over one growing season, as an AOT40 of 5 ppmh or, alternatively, as a $CUO > 1.6$ values of 4 mmol m^{-2} , based on projected leaf area.

The stomatal ozone flux can be estimated as the product of the ozone concentration close to the leaves or needles and the inverse of the sum of resistances along the ozone diffusion pathway to the site of action within the leaf interior (Ashmore et al., 2004). This resistance is a function of a number of factors, including atmospheric turbulence, canopy height and structure, species-specific phenology, and the effects of factors such as irradiance, soil moisture deficit and vapor pressure deficit on the stomatal component of the resistance.

A new deposition module has been developed and incorporated into European Modelling and Evaluation Programme (EMEP) photochemical model that uses a multiplicative simulation model to estimate stomatal conductance (Ashmore, 2003; Ashmore et al., 2004; Tuovinen, Ashmore, Emberson, & Simpson, 2004). The major advantage in using the ozone flux rather than concentration-based approaches is that the very substantial influence of climatic variables on ozone uptake is included (Ashmore et al., 2004). Contrary, the main problems with flux based approach can be attributed to uncertainties due to (1) parameterisation of stomatal conductance, (2) parameterisation of non-stomatal deposition, and (3) the representativeness of species used in flux-effects studies (Grünhage, Krupa, Legge, & Jäger, 2004).

A third concept of risk assessment has been suggested, based on maximum permissible O_3 concentrations (MPOC) to protect vegetation (Krause, Köllner, & Grünhage, 2003). The MPOC allows classification of the probability for adverse plant response to ozone exposure and defines critical mean ozone concentrations for different averaging times (Ashmore et al., 2004). The incorporation of the orography in the ozone concentration data is presented by Loibl, Winiwarter, Kopsca, Zueger, and Bauman (1994). Incorporation the altitudinal variation of the ozone concentrations in the proces of interpolation with the non linear algorithm is described in Fowler et al. (1995). The methods developed to incorporate the effects of topography into the map of rural mean ozone concentration are described in PORC (1997) and the underlying theory is examined

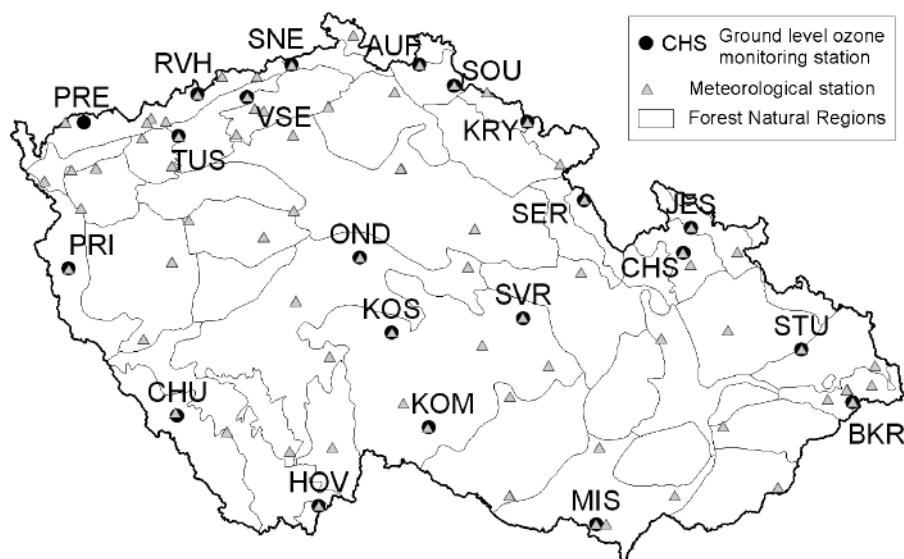


Fig. 1 Automated rural monitoring stations recording ambient ozone concentration (TUS – Tušimice, VSE – Všechny, SNE – Sníník, AUF – Albrechtice u Frýdlantu, SOU – Souš, PRE – Přebuz, STU – Studénka, JES – Jeseník, PRI – Přimda, CHU – Churáňov, HOV – Hojná Voda, OND – Ondřejov, KRY – Krkonoše Rýchory, SER – Šerlich, KOM – Kostelní

Myslová, MIS – Mikulov – Sedlec, KOS – GEMS Košetice, SVR – Svratouch, BKR – Bílý Kří, RVH – Rudolice v Horách, CHS – Ďervenohorské Sedlo) and meteorological stations for measurement of wind speed, temperature, relative humidity and global radiation on the territory of the Czech Republic

in Coyle, Smith, Stedman, Weston, and Fowler (2002).

In the Czech Republic, ambient ozone has been monitored since the early 1990s. High concentration of ozone in the atmosphere has long been observed in the Czech Republic (Hůnová, Livorová, & Ostatnická, 2003; Zapletal, 1999a, b). Negative impacts on forest ecosystems were reported (Zapletal, 1999a, b). Within the framework of annual ambient air quality assessment in the Czech Hydrometeorological Institute (CHMI) (Hůnová et al., 2003) and Ekotoxa-Centre for Environment and Land Assessment (Zapletal, 1999a, b), the AOT40 exposure index has regularly been calculated. Using the ambient ozone data recorded within a regular monitoring network in the Czech Republic, the AOT40 values for forest in vegetation periods of 1994–2001 were presented by Hůnová et al. (2003). The results indicate that the above thresholds values are generally exceeded over nearly the entire territory of the country. The results of evaluation of relationship between ozone concentration, AOT40 exposure index and the flux to coniferous forest in Hrubý Jeseník Mountains in 1998 in the Czech Republic were presented in Zapletal (1999a).

The aim of this study was to estimate ozone concentration and total and stomatal ozone fluxes to

coniferous and deciduous forest in growing season (April–September) of the year 2001 in the Czech Republic on a 1×1 km grid, to compare ozone deposition flux with the AOT40 index. Ozone deposition flux to forest was estimated from the monitored and modelled ozone concentrations in the air and from its deposition velocities. The data of ozone concentration from The Czech Hydrometeorological Institute database were used (CHMI, 2002a). Empirical methods to quantify the spatial pattern in surface concentrations at 1 km resolution, incorporating topography, are used. The procedure maps ozone concentrations during the period of the day when measurements are representative of the forest areas of countryside. The effects of boundary layer stability are quantified using the observed relationship between the diurnal variability of surface ozone concentration and an altitude. The spatial distribution of the seasonal average ozone concentration are calculated from the measurements realised in the Czech Republic. The calculated ozone concentration have spatial resolution higher than those obtained from calculations based on simulation with EMEP (Jonson, Sundet, & Tarrasón, 2001). Ozone deposition velocities were calculated according to a multiple resistance model incorporating aerodynamic resistance (R_a), laminar layer resistance (R_b) and surface resistance (R_c). The methodology we report

Table 1 Listing of daily mean ozone concentration, mean ozone concentration during the period 11–17 h UTC, during April to September 2001 and the altitude of monitoring stations

Code	Site name	Altitude (m a.s.l.)	Mean ozone concentration ($\mu\text{g m}^{-3}$) during April to September 2001	
			Daily mean	11–17 h UTC
TUS	TUŠIMICE	322	68.3	89.1
VSE	VŠECHLAPY	216	56.6	80.5
SNE	SNĚŽNÍK	588	77.1	87.6
AUF	ALBRECHTICE U FRÝDL.	535	75.4	86.5
SOU	SOUŠ	771	73.4	86.4
PRE	PŘEBUZ	904	80.5	90.9
STU	STUDÉNKA	231	58.8	84.1
JES	JESENÍK	625	77.3	85.3
PRI	PŘÍMDA	745	81.9	93.1
CHU	CHURÁČOV	1,122	87.0	93.6
HOV	HOJNÁ VODA	818	77.0	86.1
OND	ONDŘEJOV	514	76.1	88.0
KRY	KRKONOŠE RÝCHORY	1,001	82.2	86.0
SER	ŠERLICH	1,011	85.5	90.8
KOM	KOSTELNÍ MYSLOVÁ	569	80.3	95.5
MIS	MIKULOV – SEDLEC	245	77.7	94.2
KOS	KOŠETICE (GEMS)	534	71.5	87.4
SVR	SVRATOUCH	735	79.0	87.3
BKR	BÍLÝ KŘÍ	890	80.4	85.7
RVH	RUDOLICE V HORÁCH	840	84.8	93.3
CHS	ĚERVENOHORSKÉ SEDLO	1,013	87.7	91.0

in this paper includes the surface resistance (R_c) formulation of Wesely (1989), which consists of a variety of resistances added in series or in parallel within the canopy and over the soil. Surface resistance (R_c) comprises stomatal resistance (R_{sto}) which includes dependence upon global radiation and surface air temperature.

2 Material and Methods

2.1 Ozone Concentrations

Ambient ozone concentrations in the Czech Republic has been routinely monitored and evaluated since 1992 in a regular nation-wide monitoring network by The Czech Hydrometeorological Institute (CHMI, 2002a). For this study the databases of the Air Quality Information System of the Czech Republic (CHMI, 2002a) were used. At present the measurements of ozone concentration are carried out at 60 automated ambient air quality stations representing rural, mountainous and urban areas. Automatic

monitoring stations operate continuously on a 30 min time resolution. The ozone concentration measurement is based on ultraviolet absorption photometry. Some of the stations, within the meteorological monitoring framework, also record global solar radiation.

For this study, the monitoring data from rural areas (21 automated rural monitoring stations for ozone concentrations measurements and 73 meteorological monitoring stations for wind speed, global radiation, air temperature and relative humidity measurements) were used (see Fig. 1).

Ozone concentrations during the afternoon in the vegetation period, when the planetary boundary layer is well developed, were compared on the rural monitoring sites. Listing of daily mean ozone concentration, mean ozone concentration during the period 11–17 h UTC during April–September 2001 and the altitude of monitoring station are presented in Table 1.

The methods developed to incorporate the effects of topography into the map of rural mean ozone concentration are described in PORC (1997) and the underlying theory is examined in Coyle et al. (2002).

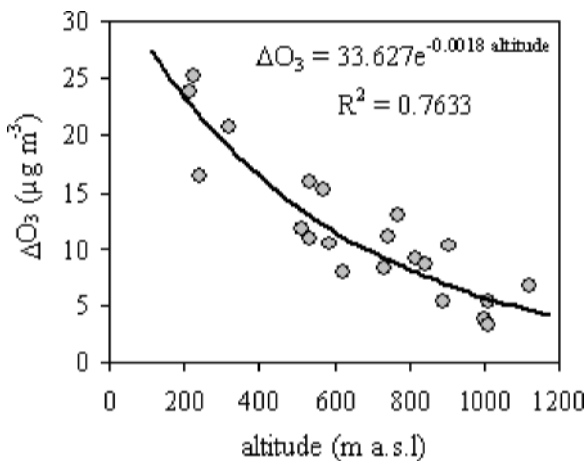


Fig. 2 Relationship of seasonal ΔO_3 (difference of seasonal 2001 average O_3 concentration in the period from 11 to 17 h UTC and seasonal 2001 24 average O_3 concentration) at rural sites to the sites altitude

The map was produced by interpolating the afternoon value of a variable from rural sites then modifying the resulting grid cell values to account for the diurnal cycle in ozone concentration. Afternoon average O_3 concentrations (the concentration during the period 11–17 h UTC) at the rural monitoring sites are interpolated across forest area ecosystems by applying a minimum curvature interpolation algorithm (Golden Software, 1999) that produces gridded data at 1×1 km resolution. Minimum curvature is used as ozone varies quite slowly across the landscape during the average period and this interpolation method provides a smooth fitted surface. For the 24 h mean ozone concentration this is done using the variable ΔO_3 (the difference between the seasonal average ozone concentration during the period 11–17 h UTC and the daily mean concentration). This variable was then related to the altitude (h) of the monitoring station. This effect is quantified in Fig. 2 as the relationship between altitude of monitoring station and ΔO_3 . The relationship :

$$\Delta O_3 = 33.627e^{-0.0018 \text{ altitude}} \quad (1)$$

was used with an altitude map of country to obtain ΔO_3 for each 1×1 km grid square of the forest area. The afternoon value in each grid square is adjusted for the diurnal cycle using relationship (1).

2.2 Exposure Index AOT40

Using the ambient ozone data recorded within a regular monitoring network in the Czech Republic, the AOT40

values for vegetation in 2001 were presented by CHMI (2002b). AOT40 – accumulated exposure was calculated as the sum of the difference between hourly ozone concentrations and thresholds level 40 ppb for each hour when this threshold value was exceeded. Pursuant to the requirements of the Directive 2002/3/EC (EC, 2002), AOT40 was calculated for the period of 3 months (May–July) measured between 8 and 20 h Central European Time (7 and 19 h UTC).

2.3 Ozone Deposition Flux

2.3.1 Description and Application of the Ozone Deposition Flux Model

Since no simple method was available for direct measurement of ozone deposition flux, the deposition flux was estimated from measured concentrations of ozone in air multiplied by the corresponding deposition velocities:

$$F = V_d(z)C(z) \quad (2)$$

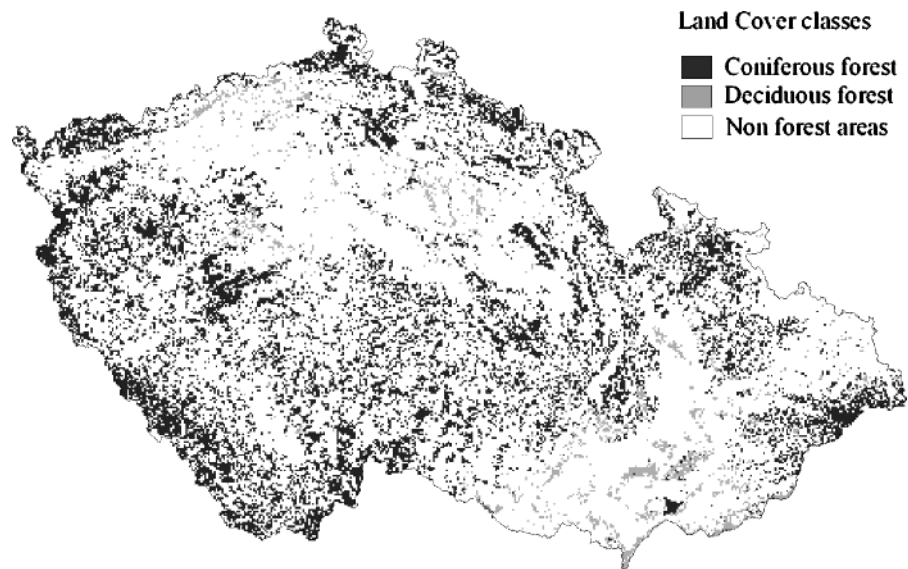
where F is the deposition flux of the component to a unit area (e.g. m^2), V_d is the deposition velocity of the ozone and $C(z)$ is concentration of the ozone at a height z above surface.

The ozone deposition model differentiates between stomatal and non-stomatal deposition components and estimates ozone deposition according to vegetation-specific parameterisation. Deposition velocity for ozone was calculated using the resistance analogy. Deposition velocity V_d may be expressed by the inverse of sum of three resistances:

$$V_d(z) = \frac{1}{R_a(z) + R_b + R_c} \quad (3)$$

The three resistances represent three stages of transport: the aerodynamic resistance, R_a , for the turbulent layer, the laminar layer resistance, R_b , for the quasi-laminar layer, the surface or canopy resistance, R_c , for the receptor itself. In this study the aerodynamic resistance, R_a , is calculated from micrometeorological relations suggested by Voldner, Barrie, and Sirois (1986) and Hicks, Baldocchi, Meyers, Hosker, & Matt (1987) and the quasi-laminar layer resistance, R_b , is calculated from micrometeorological relations suggested by Hicks et al. R_a and R_b may be assessed on basis of known wind velocity and a

Fig. 3 Land cover on the territory of the Czech Republic on 1×1 km grid (coniferous and deciduous forest)



surface roughness. The annual average values of the surface roughness, z_0 , for different surface types were derived from the literature (Erisman & Draaijers, 1995; Voldner et al.). Annual averages of the surface roughness, z_0 , were related to the corresponding surface characteristics on the forest territory of the Czech Republic according to the CORINE Land Cover classes (EEA, 2000). Land Cover classes used were coniferous forest (*Picea abies*) and deciduous forest (*Fagus sylvatica*) (see Fig. 3).

The surface resistance (R_c) comprises the plant canopy (described using a “big leaf” formulation) and the underlying soil. Surface resistance was calculated using the following equation:

$$R_c = \left(\frac{1}{R_{sto} + R_m} + \frac{1}{R_{inc} + R_{soil}} + \frac{1}{R_{ext}} \right)^{-1} \quad (4)$$

R_c was calculated on basis of known global radiation, surface temperature, relative humidity, land cover according to Eq. 4 using the results and

assumption obtained from literature (Table 2) for calculating and parameterization of the land-cover specific canopy stomatal resistance (R_{sto}), the mesophyll resistance (R_m), the canopy cuticle or external leaf resistance (R_{ext}), the soil resistance (R_{soil}), and the incanopy resistance (R_{inc}), respectively. The stomatal resistance (R_{sto}) includes dependence upon global radiation and surface air temperature. Here we use the following generalized function to estimate the canopy stomatal resistance (Wesely, 1989):

$$R_{sto} = R_i \left\{ 1 + \left[200(G + 0.1)^{-1} \right]^2 \right\} \left\{ 400[T_s(40 - T_s)]^{-1} \right\} \quad (5)$$

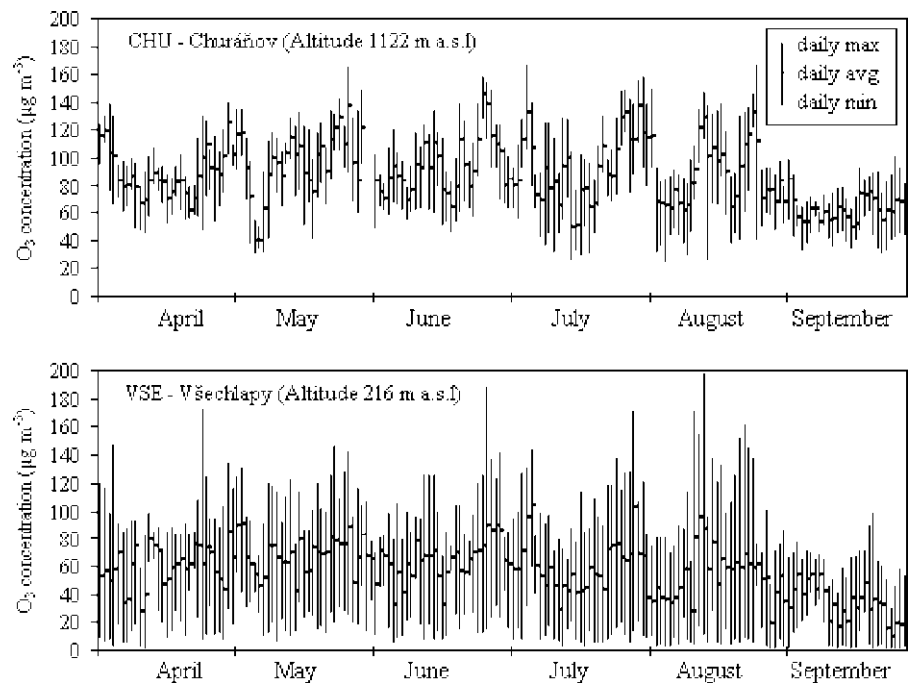
where R_i is input resistance in $s\ m^{-1}$, G is the global radiation in $W\ m^{-2}$ and T_s is the surface air temperature ($^{\circ}C$). We only extract values of R_i from Wesely’s (1989) table that are pertinent to the present study (Table 2).

Table 2 Vegetation – specific parameters used in the ozone deposition model

Parameter	Coniferous forest	Coniferous forest References	Deciduous forest	Deciduous forest References
LAI	8.6	Erisman & Draaijers (1995)	5	Meyers and Baldocchi (1988)
R_i ($s\ cm^{-1}$)	2.5	Wesely (1989)	1.4	Wesely (1989)
R_m ($s\ cm^{-1}$)	0	Wesely (1989)	0	Wesely (1989); Lagzi et al. (2004)
R_{soil} ($s\ cm^{-1}$)	3 ^a	Brook, Zhang, Di-Giovanni, and Padro (1999)	3	Brook et al. (1999)
R_{ext} ($s\ cm^{-1}$)	20 ^a	Brook et al. (1999)	20	Brook et al. (1999)

^a For mixed forest

Fig. 4 Daily maximum and minimum hourly average ozone concentrations for each day of summer months (April–September) of 2001 at two rural monitoring sites: Všeclapy (VSE) near Krušné hory Mts. and Churáňov (CHU) in Šumava Mts



The incanopy resistance (R_{inc}) for vegetation was modelled with (van Pul & Jacobs, 1994):

$$R_{inc} = bLAIh/u_* \quad (6)$$

where LAI is the one leaf area index, h the vegetation height, b an empirical constant taken as 14 m^{-1} and u_* is a friction velocity. The current parameterization that was used to calculate the surface resistance (R_c) for coniferous forest (*P. abies*) and deciduous forest (*F. sylvatica*), is summarised in Table 2.

Here we present calculations for growing season in 2001. The resistance model of the ozone deposition velocities calculation under conditions on the forest territory of the Czech Republic was applied as follows: the forest area of the Czech Republic was divided into 41 forest natural regions, and the seasonal average horizontal wind velocity, u_z , for the growing season (April–September) in the year 2001 at 73 meteorological stations, was extrapolated for all these regions. The value R_a and value R_b were calculated from the micrometeorological relations by Voldner et al. (1986) and Hicks et al. (1987) by using the average value, z_0 , according to individual surface types and seasonal average values, u_z , in the different regions.

The seasonal average deposition velocities, $V_d(z)$, of ozone at a 10 m reference height for individual surfaces (grid cells $1 \times 1 \text{ km}$), represented in regions surrounding the 73 meteorological stations on the

Czech forest territory were calculated by diurnal averages of the values R_a , R_b and R_c from Eq. 3. Each grid cell ($1 \times 1 \text{ km}$) was assigned the dominant surface type.

Seasonal average value of ozone deposition flux, FO_3 , was calculated from seasonal average concentration, $C(z)$, seasonal average deposition velocity, $V_d(z)$, and time, t , in a $1 \times 1 \text{ km}$ grid resolution.

3 Results and Discussion

3.1 Ozone Concentrations

The hourly mean ground level concentration of ozone in rural sites in the Czech Republic vary between 0 and $200 \mu\text{g m}^{-3}$, but generally lie in the range $50\text{--}100 \mu\text{g m}^{-3}$. To illustrate the course (variability) in time and between contrasting rural sites, data for two monitoring stations are presented in Fig. 4.

These data provide the maximum and minimum hourly concentration for each day of the growing season (April–September). Days with a concentration maxima exceeding $100 \mu\text{g m}^{-3}$ can be taken to imply photochemical episodes, when the ozone concentration is raised above background level by a combination of antropogenic precursor emissions and weather conditions.

Fig. 5 The effects of altitude on ozone concentration at **a** Tušimice (TUS) and Rudolice (RVH) and **b** Studénka (STU) and Bílý Kříž (BKR) during April–September 2001

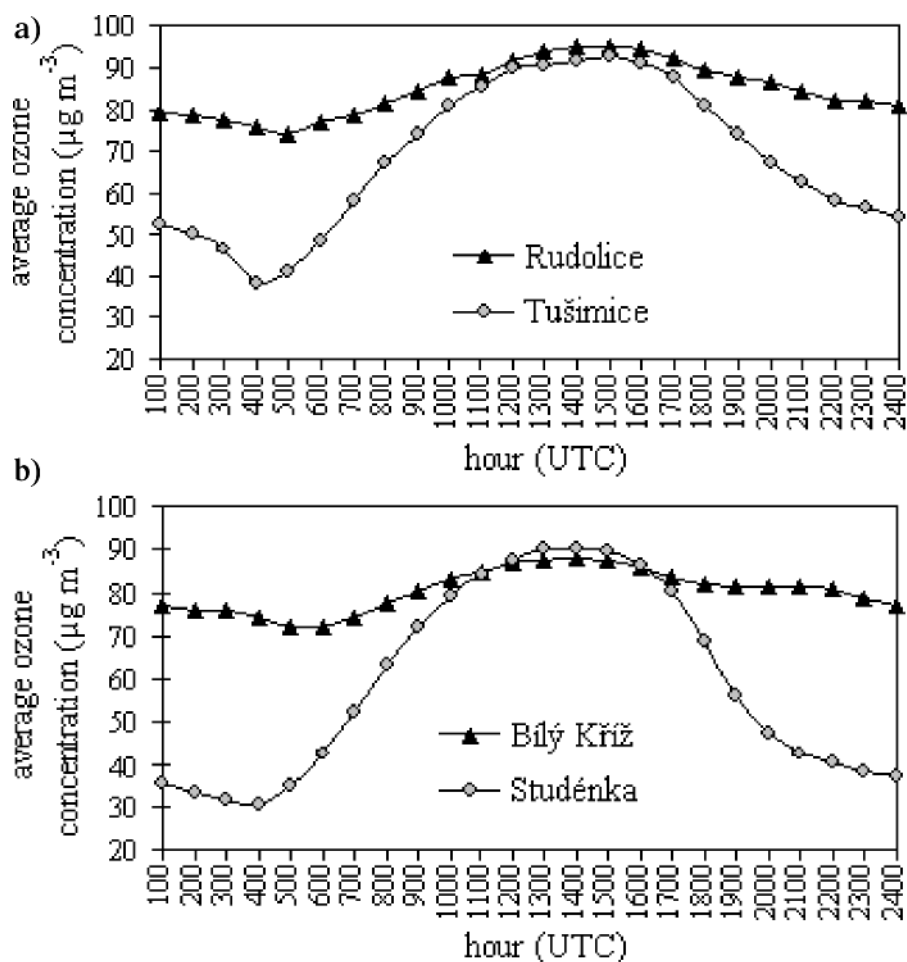
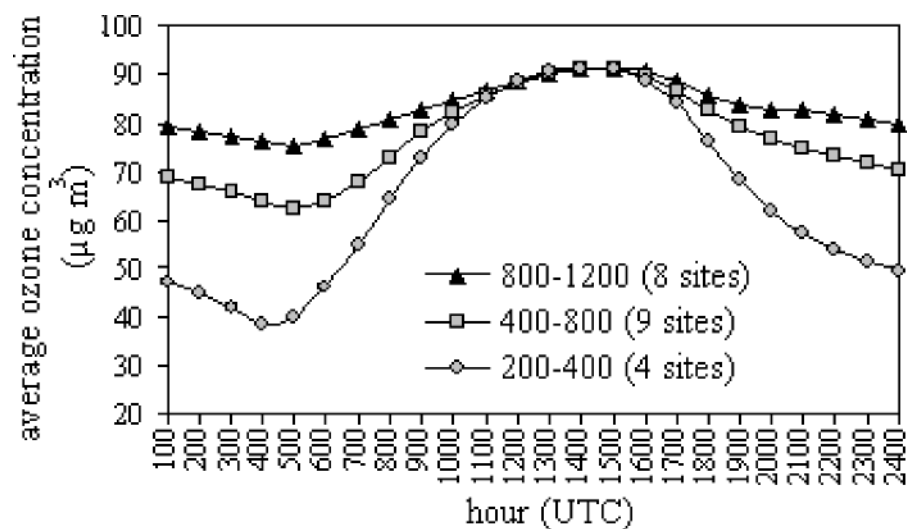


Fig. 6 Diurnal cycles at rural monitoring stations during April–September 2001, averaged into three groups by site altitude



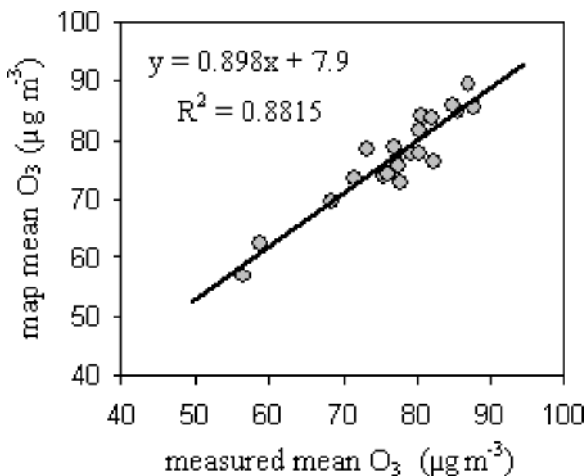


Fig. 7 Plot of the measured daily mean ozone concentration during April–September 2001 versus the estimated values in the grid squares containing the monitoring site

3.1.1 Effects of Altitude on Ozone Concentration

The effects of wind on ozone concentration are to reduce the effects of depletions at the ground on surface concentrations. As wind speeds and turbulent mixing processes are enhanced on hills, it follows that surface depletion effects are less on hills than sheltered lowland sites. The effects are illustrated by neighbouring monitoring stations which differ substantially in an altitude, as in an example Studénka (STU) and Bílý Kří (BKR) (The Beskydy Mts.) differ by 659 m in the vertical yet are within 39 km horizontally. These show almost identical concentrations during the period 11–17 h UTC (respectively 12–18 h CET) in growing season while the night time concentrations differ by 40% or more. The same effects may be observed in data from Rudolice (RVH) and Tušimice (TUS) (The Krušné Mts.), sites separated by 24 km in the horizontal and about 518 m in the vertical, (Fig. 5).

Diurnal average cycles at rural monitoring stations during April–September 2001, plotted in three groups by site altitude are shown in Fig. 6.

The magnitude and timing of mid-afternoon peak is very similar at all sites, showing that rural concentrations are generally comparable over a wide geographical area during this period. The diurnal cycles in ozone for summer period show that during the afternoon many of the monitoring stations in the same region (within 100 km of each other), show similar concentrations despite considerable altitude differences within the boundary layer. These effects

may be seen in whole rural monitoring network in the Czech Republic. Similar effects on rural areas in the United Kingdom were described by PORG (1997) and Coyle et al. (2002). The very similar concentrations during the afternoon period of the day with the most effective vertical mixing for neighbouring rural monitoring stations show that during this period the rural monitoring stations are providing data which are representative of a much larger geographical area than during the night when local effects of shelter etc. generate great horizontal variability.

3.1.2 Mapping of Mean Ozone Concentrations During Growing Season

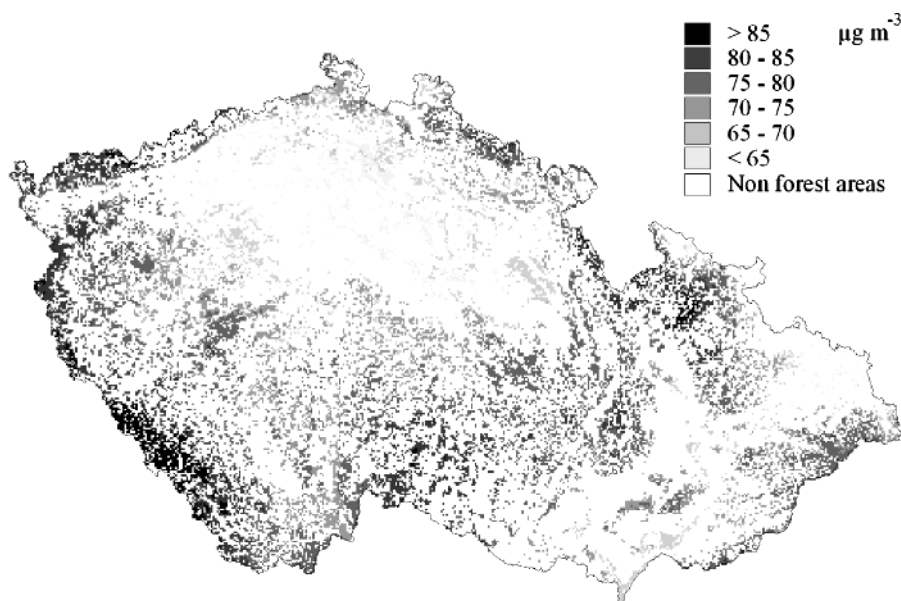
Out of all 60 monitoring stations over the Czech Republic territory, only the 21 monitoring stations located within rural areas were included in the calculations. Ozone values recorded at urban stations were considered to be not relevant for forest areas. The rural monitoring network contains 21 sites to define the spatial patterns and simple direct interpolation between the sites fails to predict the pronounced effect of topography on the pattern of surface ozone concentration.

The attribute of the minimum-curvature algorithm is a tendency to maintain the recorded values at the monitoring stations as much as possible. The ozone concentration is generally influenced by the orography (Coyle et al., 2002; Fowler et al, 1995; Loibl et al., 1994; PORG, 1997). The incorporation of an altitude enhancement at 1×1 km scale (according to PORG (1997)) provides a realistic picture of the variation in ozone concentration with undulating topography of the Czech Republic. In the case of the seasonal average ozone concentration, there is perfect agreement between measurements and the map (Fig. 7).

Spatial distribution of mean ozone concentration over forest territory in the Czech Republic in April–September is shown in Fig. 8. Ozone concentration values are ranging from 54 to 92 $\mu\text{g m}^{-3}$. Mean ozone concentration is 76 $\mu\text{g m}^{-3}$.

The highest values of ozone concentrations were recorded in borderline mountain regions (higher altitudes), in the Krušné Mts. in northwest part of the country, the Orlické Mts. and Jeseníky Mts. in the northern part of the country, the Šumava Mts. in the south, the Beskydy Mts. in the eastern and central parts of the Czech-Moravian Highlands. Climatic

Fig. 8 Mean ozone concentration ($\mu\text{g m}^{-3}$) in forest in the Czech Republic on a 1×1 km grid in April–September 2001

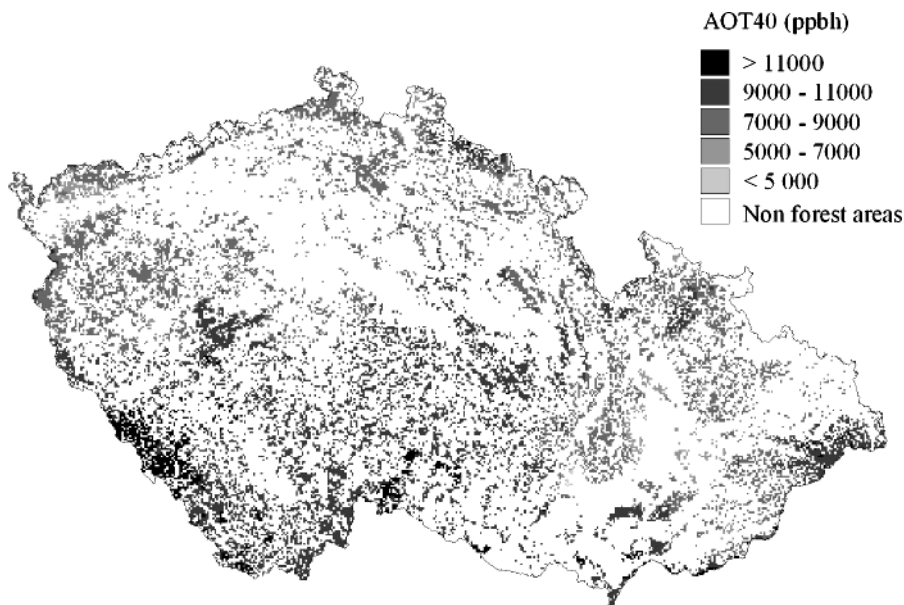


conditions in higher altitudes differ from those in lower altitudes. The locations in higher altitudes are more exposed to ground ozone and are less affected by night inversion conditions. Thus the concentration values of ground ozone in the open grow up with increasing altitude. The highest values of ozone concentrations were localised in higher altitudes of mountain areas.

3.2 Exposure Index AOT40

Using the ambient ozone data recorded within a regular monitoring network in the Czech Republic, the AOT40

Fig. 9 Fields of AOT40 ambient ozone exposure index for forests (ppbh) in the Czech Republic on a 1×1 km grid in May–July 2001 (CHMI, 2002a)



values for forest in vegetation periods of 2001 were presented by CHMI (2002b). Spatial distribution of AOT40 over forest territory in the Czech Republic on a 1×1 km grid in May–July is shown in Fig. 9. The AOT40 values range from 3167 ppbh to 14296 ppbh. Mean AOT40 value is 9,107 ppbh. The AOT40 threshold level of 9,000 ppbh for vegetation was exceeded on over 50% of the forested territory in Czech Republic in 2001. The highest AOT40 values were recorded in mountain regions (higher altitudes), in the Krkonoše Mts. and Jeseníky Mts. in the northern part of the country, the Šumava Mts. (highest AOT40

Fig. 10 Mean total and stomatal fluxes of ozone ($\text{nmol m}^{-2} \text{s}^{-1}$) to forest in the Czech Republic on a 1×1 km grid in April–September 2001

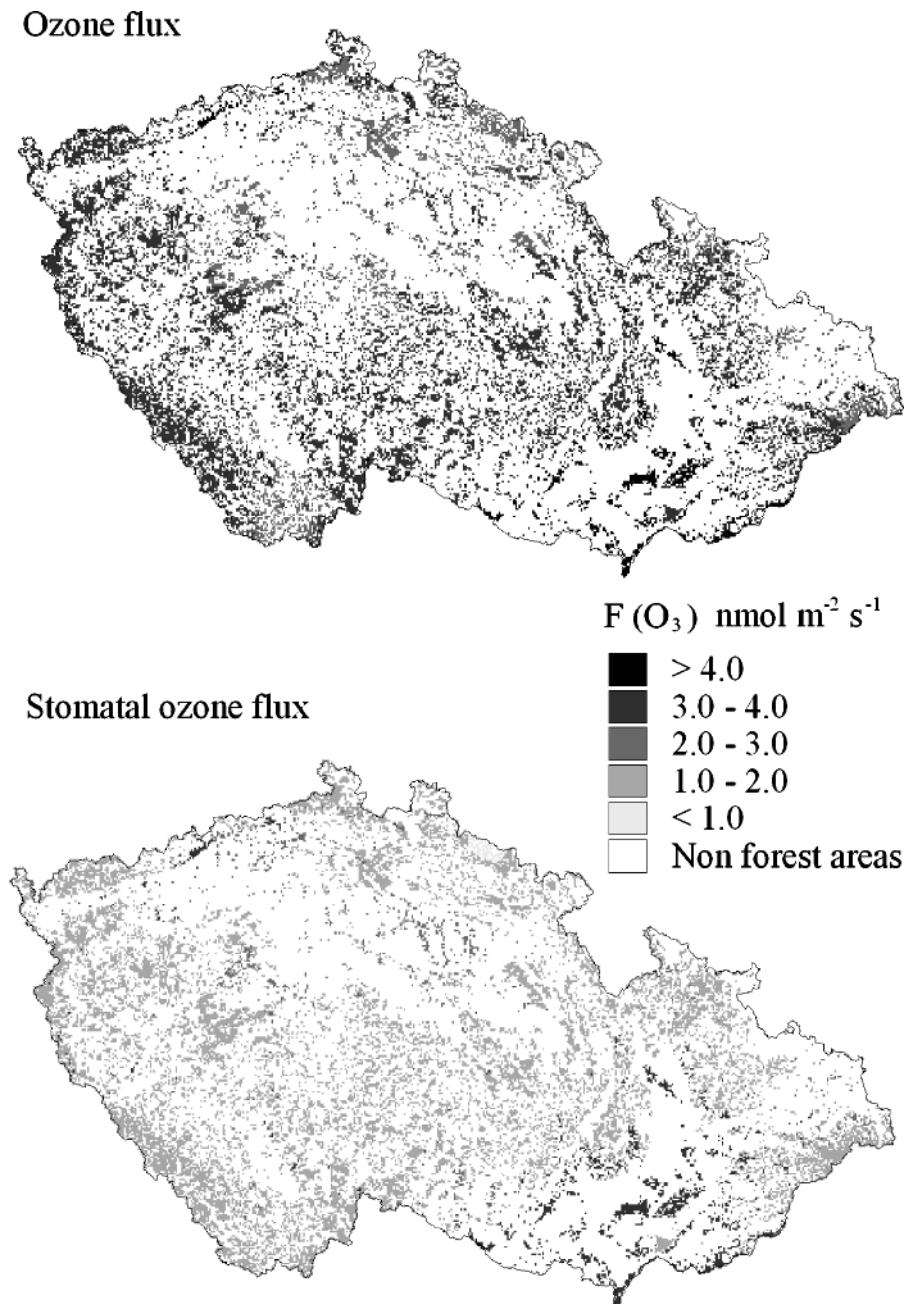


Table 3 Ozone deposition model statistics for coniferous and deciduous forest in the Czech Republic

Surface	Ozone flux ($\text{nmol m}^{-2} \text{s}^{-1}$)			Stomatal ozone flux ($\text{nmol m}^{-2} \text{s}^{-1}$)			Deposition velocity (cm s^{-1})		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Spruce	3.14	2.23	3.68	1.65	0.59	2.03	0.24	0.1	0.6
Beech	4.22	2.74	5.1	3.05	1.81	3.83	0.32	0.1	0.75

Table 4 Comparison of observed and modelled dry-deposition velocities (cm s^{-1})

Surface	Observation				Model calculation for Czech Republic		
	Mean	Range	Reference	Condition	Mean	Range	Condition
Spruce		0–0.7	Pilegaard, Jensen, and Hummelshoj (1995a)	June	0.24	0.1–0.6	April–September
Beech	0.4	0.1–0.7	Pilegaard, Jensen, and Hummelshoj (1995b)	April–May	0.32	0.1–0.75	April–September

values in the Czech Republic) in the southern, the Beskydy Mts. in the eastern and south parts of the Czech-Moravian Highlands.

3.3 Ozone Deposition Flux

Spatial distribution of mean total and stomatal fluxes of ozone to coniferous and deciduous forest over the Czech Republic in April–September is shown in Fig. 10. The highest values of total and stomatal fluxes of ozone were localised in higher altitudes of mountain areas, Jeseníky Mts. in the northern part of the country, in Krušné Mts. in north-west, Ěeský les Mts. in west, the Beskydy Mts. in the eastern and south-eastern parts of the Czech-Moravian Highlands.

Ozone deposition model statistics are presented in Table 3.

The share of stomatal ozone flux on total ozone flux makes 53% in coniferous forest, while 72% in deciduous forest. Calculated deposition velocities of ozone for coniferous and deciduous forest were compared with observations based on data from literature (Table 4). The modelled data are in good agreement with observed ones.

3.4 Comparison of Index Exposure AOT40 and Ozone Deposition Flux

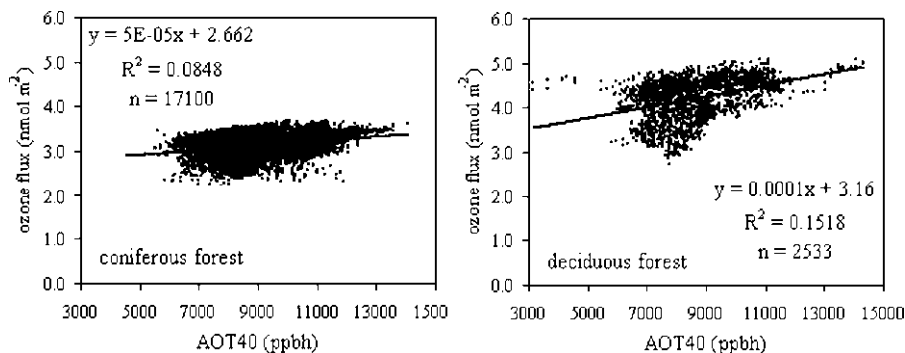
Considering the potential impacts of ozone on forest the knowledge of the responses of nation-wide

species composition is of primary importance. Forested area roughly accounted for 33.4% of the Czech Republic territory by the year 2000 (BFH, 2001). Forest tree species composition has remained highly stable over the last 30 years with the major share being spruce *P. abies* (54% in 2000), followed by pine *Pinus sylvestris* (17.6% in 2000). The share of mixed oak *Quercus* accounts for 6.3% and European beech *F. sylvatica* for 6.0%.

Regression analysis of total ozone flux (April–September) in relation to AOT40 exposure index (May–July) on 1×1 km grid on the forest territory of the Czech Republic is shown in Fig. 11.

There is significant correspondence between the exposure index AOT40 and the total ozone flux, but the relation between the total ozone flux and AOT40 exposure index is not clear in all parts of the forest territory. The high values of exposure index AOT40 do not correspond with the high values of total ozone flux in some parts of the territory of the Czech Republic (see Figs. 9 and 10). Emberson et al. (2000b) present differences in the spatial distribution between stomatal flux and exposure index AOT40 modelled for beech on a European scale and indicate important implications for risk analysis. If AOT40 had been used as a basis for assessing risk, the highest values would be found in central Europe; in contrast, values of the flux indices in central Europe were either comparable to, or lower than, those in the other grid squares (Emberson et al., 2000b).

Fig. 11 Regression analysis of total ozone flux (April–September) in relation to AOT40 exposure index (May–July) on 1×1 km grid on the forest territory of the Czech Republic in 2001. Both correlations are significant at the $p < 0.01$ level



4 Conclusions

Modelling of ozone concentrations and deposition to a coniferous and deciduous forest on 1×1 km grid has been described in this study for the territory of the Czech Republic. The deposition has been assessed from the measured and modelled concentrations of ozone in the atmosphere. The effects of boundary layer stability were quantified using the observed relationship between the diurnal variability of surface ozone concentration and altitude. Climatic conditions in higher altitudes differ from those in lower altitudes. The locations in higher altitudes are more exposed to ground ozone and are less affected by night inversion conditions. Thus the concentration values of ground ozone in the open grow up with increasing altitude of mountain areas of the Czech Republic.

The results of AOT40 values presented for 2001 indicate that measured ambient ozone concentrations in the Czech Republic exceeded the critical levels set for ozone almost over the 50% forest territory. It seems that patterns of exposure index AOT40 and pattern of ozone deposition flux are similar in major parts of the forest territory of the Czech Republic. The differences between index exposure AOT40 and ozone deposition fluxes in some parts of forest territory in the Czech Republic can be largely due to the facts that in central Europe, the meteorological conditions favour ozone formations (high temperatures and high vapour-pressure deficits) tend to inhibit stomatal conductance and hence uptake (Simpson et al., 2003).

Acknowledgement This study was funded by the Ministry of Environment of the Czech Republic (project VaV/740/1/02).

References

- Ashmore, M. (2003). How well can we model ozone fluxes? A report from the harrogate ad-hoc expert panel meeting on modelling and mapping ozone flux and deposition to vegetation. In P. E. Karlsson, G. Sellden, & H. Pleijel (Eds.), *Establishing Ozone Critical Levels II*, UNECE Workshop Report, IVL report B 1523 (pp. 40–45). Gothenburg, Sweden: IVL Swedish Environmental Research Institute.
- Ashmore, M., Emberson, L., Karlsson, P. E., & Pleijel, H. (2004). New directions: A new generation of ozone critical levels for the protection of vegetation in Europe. *Atmospheric Environment*, 38, 2213–2214.
- Ashmore, M., Emberson, L., Karlsson, P. E., & Pleijel, H. (2005). New directions: Discussion of “A new generation of ozone critical levels for the protection of vegetation in Europe” by Ashmore et al. – Further response. *Atmospheric Environment*, 39, 5214–5215.
- BFH (2001). *Forest condition in Europe*. Executive report, UN-ECE and EC, Geneva and Brussels.
- Brook, J. R., Zhang, L., Di-Giovanni, F., & Padro, J. (1999). Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part I: model development. *Atmospheric Environment*, 33, 5037–5051.
- Bull, K. R., Karlsson, P. E., Sellden, G., & Pleijel, H. (2003). Workshop summary. In P. E. Karlsson, G. Sellden, & H. Pleijel (Eds.), *Establishing Ozone Critical Levels II*, UNECE Workshop Report, IVL report B 1523 (pp. 9–13). Gothenburg, Sweden: IVL Swedish Environmental Research Institute.
- CHMI (2002a). *Air pollution and atmospheric deposition in data, the Czech Republic 2001* (345 pp.). Prague: Czech Hydrometeorological Institute <http://www.chmi.cz>.
- CHMI (2002b). *Air pollution in the Czech Republic in 2001* (161 pp.). Prague: Czech Hydrometeorological Institute.
- Coyle, M., Smith, R. I., Stedman, J. R., Weston, K. J., & Fowler, D. (2002). Quantifying the spatial distribution of surface ozone concentration in the UK. *Atmospheric Environment*, 36, 1013–1024.
- EC (2002). Directive 2002/3/EC of the European Parliament and the Council of the European Union of 12 February 2002 relating to ozone in ambient air.
- EEA (2000). Corine land cover 2000 vector by country (CLC2000). Vector for the Czech Republic. European Environmental Agency data service. <http://dataservice.eea.eu.int/>.
- Emberson, L. D., Simpson, D., Tuovinen, J.-P., Ashmore, M. R., & Cambridge, H. M. (2000a). *Towards a model of ozone deposition and stomatal uptake over Europe*. EMEP MSC-W Note 6/2000, 1–57.
- Emberson, L. D., Ashmore, M. R., Cambridge, H. M., Simpson, D., & Tuovinen, J.-P. (2000b). Modelling stomatal ozone flux across Europe. *Environmental Pollution*, 109, 403–414.
- Emberson, L. D., Wieser, G., & Ashmore, M. R. (2000c). Modelling of stomatal conductance and ozone flux of Norway spruce: Comparison with field data. *Environmental Pollution*, 109, 393–403.
- Emberson, L. D., Ashmore, M. R., Simpson, D., Tuovinen, J.-P., & Cambridge, H. (2001). Modelling and mapping ozone deposition in Europe. *Water, Air, and Soil Pollution*, 130, 577–582.
- Erismann, J. W., & Draaijers, G. P. J. (1995). *Atmospheric deposition in relation to acidification and eutrophication*. Amsterdam, The Netherlands: Elsevier.
- Fowler, D., Smith, R. I., Coyle, M., Weston, K. J., Davies, T. D., & Ashmore, M. R., et al. (1995). Quantifying the fine scale (1 km×1 km) exposure and effects of ozone. Part 1. Methodology and application for effects on forests. *Water, Air, and Soil Pollution*, 85, 1479–1484.
- Fuhrer, J., & Achermann, B. (Eds.) (1994). Critical levels for opzone. A UN ECE workshop report, Schriftenreihe der FAC No.16, Bern-Liebfeld.

- Fuhrer, J., Skarby, L., & Ashmore, M. R. (1997). Critical levels for ozone effects on vegetation in Europe. *Environmental Pollution*, 97, 91–106.
- Fuhrer, J. (2000). Introduction to the special issue on ozone risk analysis for vegetation in Europe. *Environmental Pollution*, 109, 359–360.
- Golden Software (1999). *Surfer: User's guide. Contouring and 3D surface mapping for scientists and engineers*. Colorado, USA: Golden Software.
- Grünhage, L., Krupa, S. V., Legge, A. H., & Jäger, H.-J. (2004). Ambient flux-based critical values of ozone for protecting vegetation: Differing spatial scales and uncertainties in risk assessment. *Atmospheric Environment*, 38, 2433–2437.
- Hicks, B. B., Baldocchi, D. D., Meyers, T. P., Hosker Jr., R. P., & Matt, D. R. (1987). A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. *Water, Air, and Soil Pollution*, 36, 311–330.
- Hůnová, I., Livorová, H., & Ostatnická, J. (2003). Potential ambient ozone impact on ecosystems in the Czech Republic as indicated by exposure index AOT40. *Ecological Indicators*, 3, 35–47.
- Jonson, J. E., Sundet, J. K., & Tarrasón, L. (2001). Model calculation of present and future levels of ozone and ozone precursors with a global and a regional model. *Atmospheric Environment*, 35, 525–537.
- Karlsson, P. E., Selldén, G., & Pleijel, H. (Eds.) (2003). Establishing ozone critical levels II. In *2003, UNECE Workshop Report, IVL report B 1523*. Gothenburg, Sweden: IVL Swedish Environmental Research Institute.
- Karlsson, P. E., Uddling, J., Braun, S., Broadmeadow, M., Elvira, S., & Gimeno, B. S., et al. (2004). New critical levels for ozone effects on young trees based on AOT40 and simulated cumulative leaf uptake of ozone. *Atmospheric Environment*, 38, 2283–2294.
- Kärenlampi, L., & Skärby, L. (Eds.) (1996). Critical levels for ozone in Europe: Testing and finalizing the concepts. *UNECE workshop report* (363 pp.). Kuopio: Univ. of Kuopio, Dept. of Ecology and Environmental Science.
- Krause, G. H. M., Köllner, B., & Grünhage, L. (2003). Effects of ozone on European forest trees species – A concept of local risk evaluation within ICP-forests. In P. E. Karlsson, G. Selldén, & H. Pleijel (Eds.), *Establishing ozone critical levels II, UNECE workshop report, IVL report B 1523* (pp. 230–235). Gothenburg, Sweden: IVL Swedish Environmental Research Institute.
- Krause, G., Köllner, B., Grünhage, L., Jäger, H.-J., Bender, J., & Weigel, H.-J. (2005a). New directions: Discussion of “A new generation of ozone critical levels for the protection of vegetation in Europe” by Asmore et al. – Comments. *Atmospheric Environment*, 39, 5213–5214.
- Krause, G., Köllner, B., Grünhage, L., Jäger, H.-J., Bender, J., & Weigel, H.-J. (2005b). New directions: Discussion of “A new generation of ozone critical levels for the protection of vegetation in Europe” by Asmore et al. – Further response. *Atmospheric Environment*, 39, 5216–5217.
- Lagzi, I., Mészáros, R., Horváth, L., Tomlin, A., Weidinger, T., & Turányi, T., et al. (2004). Modelling ozone fluxes over Hungary. *Atmospheric Environment*, 38, 6211–6222.
- Loibl, W., Winiwarter, W., Kopsca, A., Zueger, J., & Bauman, R. (1994). Estimating the spatial distribution of ozone concentrations in complex terrain. *Atmospheric Environment*, 28, 2557–2566.
- Matyssek, R., Wieser, G., Nunn, A. J., Kozovits, A. R., Reiter, I. M., & Heerdt, C., et al. (2004). Comparison between AOT40 and ozone uptake in forest trees of different species, age and site conditions. *Atmospheric Environment*, 38, 2271–2281.
- Meyers T. P., & Baldocchi, D. D. (1988). A comparison of models for deriving dry deposition fluxes of O₃ and SO₂ to a forest canopy. *Tellus*, 40B, 270–284.
- Pilegaard, K., Jensen, N. O., & Hummelshøj, P. (1995a). Seasonal and diurnal variation in the deposition velocity of ozone over a spruce forest in Denmark. *Water, Air, and Soil Pollution*, 85, 2223–2228.
- Pilegaard, K., Jensen, N. O., & Hummelshøj, P. (1995b). Deposition of nitrogen oxides and ozone to Danish forest sites. In G. J. Heij, & J. W. Erisman (Eds.), *Acid rain research: Do we have enough answers?* (pp. 31–40). Amsterdam, The Netherlands: Elsevier.
- PORG (1997). *Ozone in the United Kingdom 1997, fourth report of the United Kingdom photochemical oxidants review group*. London: Department of the Environment.
- van Pul, W. A. J., & Jacobs, A. F. G. (1994). The conductance of a maize crop and the underlying soil to ozone under various environmental conditions. *Boundary-layer Meteorology*, 69, 83–99.
- Simpson, D., Ashmore, M., Emberson, L., Tuovinen, J.-P., MacDougall, M., & Smith, R. I. (2003). Stomatal ozone uptake over Europe: Preliminary results. In P. E. Karlsson, G. Selldén, & H. Pleijel (Eds.), *Establishing ozone critical levels II, UNECE workshop report, IVL report B 1523* (pp. 66–73). Gothenburg, Sweden: IVL Swedish Environmental Research Institute.
- Tuovinen, J.-P., Ashmore, M. R., Emberson, L. D., & Simpson, D. (2004). Testing and improving the EMEP ozone deposition module. *Atmospheric Environment*, 38, 2373–2385.
- UNECE (1988). *UN-ECE critical levels workshop report*, Bad Harzburg.
- UNECE (2005). *The condition of forests in Europe. 2005, Executive report, UNECE, Geneva* (33 pp.).
- Voldner, E. C., Barrie, L. A., & Sirois, A. (1986). A literature review of dry deposition of oxides of sulphur and nitrogen with emphasis on long-range transport modelling in North America. *Atmospheric Environment*, 20, 2101–2123.
- Wesely, M. L. (1989). Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment*, 23, 1293–1304.
- Zapletal, M. (1999a). Vztah mezi imisními koncentracemi a depozičním tokem přizemního ozonu do lesní vegetace. *Ochrana ovzduší*, 11, 4–8 (in Czech).
- Zapletal, M. (1999b). Hodnocení expozičního indexu AOT40 pro lesní ekosystém v oblasti ěervenohorského sedla (Hrubý Jeseník). In Holoubková (Ed.), *Program a sborník konference Ovzduší '99, Brno, 7.–10. 2. 1999* (pp. 172–175). Brno: Masarykova univerzita v Brně. (in Czech)

Impact of Harvest Intensity on Long-Term Base Cation Budgets in Swedish Forest Soils

Cecilia Akselsson · Olle Westling · Harald Sverdrup ·
Johan Holmqvist · Gunnar Thelin · Eva Uggla ·
Gunnar Malm

Received: 14 June 2005 / Accepted: 27 March 2006 / Published online: 19 January 2007
© Springer Science + Business Media B.V. 2007

Abstract The effects of harvesting on the long-term mass balances of calcium (Ca), magnesium (Mg) and potassium (K) were evaluated on a regional level in Sweden. A new high-resolution weathering database was used together with estimates of total deposition, losses through harvest and leaching. Estimates were made for pine and spruce separately and for two harvesting intensity scenarios: stem harvesting and whole-tree harvesting. The mass balance calculations showed net losses of Ca and Mg in almost the whole country for both scenarios. The losses were smaller for pine than for spruce. The K balances were mainly positive for pine but negative for spruce. Leaching was a main factor in the mass balances, especially for Ca and Mg. Whole-tree harvesting in spruce forests led to substantially higher net losses of K and Ca than

stem harvesting, according to the calculations. In the whole-tree harvesting scenario in spruce forests the estimated yearly net losses of Ca, Mg and K corresponded to at least 5%, 8% and 3% of the pools of exchangeable base cations, respectively, at 25% of the analysed sites. If losses of this magnitude continue the depletion of the pools of Ca, Mg and K may lead to very low base saturation of the soils, possibly accompanied by negative effects on soil fertility, runoff water quality, tree vitality and tree growth within a forest rotation in parts of Sweden. Avoiding whole-tree harvesting can improve the situation substantially for K, but the losses of Ca and Mg will still be significant.

Keywords base cations · calcium · forest soils · forestry · magnesium · pine · potassium · spruce · Sweden · harvesting

C. Akselsson (✉) · O. Westling · G. Malm
IVL Swedish Environmental Research Institute,
P. O. Box 5302, 400 14 Gothenburg, Sweden
e-mail: cecilia.akselsson@ivl.se

H. Sverdrup · G. Thelin
Department of Chemical Engineering,
Lund Institute of Technology, Lund, Sweden

J. Holmqvist
SWECO International AB, Malmö, Sweden

E. Uggla
Kalmar University,
Kalmar, Sweden

1 Introduction

The base cations calcium (Ca), magnesium (Mg) and potassium (K) are important nutrients in forest ecosystems. Together with the base cation sodium (Na) they also determine the base saturation, and they are thus critical for soil resistance to acidification. The effect of harvesting on base cation budgets is currently of great interest in Sweden since biofuels from slash are interesting as an alternative to fossil

fuels. Regional base cation budgets for different harvesting scenarios are important in decision-making processes. Base cation budget calculations on a regional scale have been implemented in Finland (Joki-Heiskala et al., 2003) and Sweden (Olsson, Rosén, & Melkerud, 1993; Sverdrup & Rosén, 1998). Since the calculations were made in Sweden new high-resolution soil geochemistry data have become available and methods for weathering rate calculations have been developed (Akselsson, Holmqvist, Alveteg, Kurz, & Sverdrup, 2004). The aims of this study were to estimate, on a regional scale, the effects of stem- and whole-tree harvesting in spruce and pine forests on the base cation budget in Swedish forest soils, to compare the budgets with the supply of exchangeable base cations in the soil, and to discuss the results in terms of sustainable forestry.

2 Materials and Methods

The basic methods employed in the study were mass balance modelling and modifications of existing regional databases. The net change (Δ) of the pool of the base cation 'i' was calculated as:

$$\Delta_i = \text{Deposition}_i + \text{Weathering}_i - \text{Harvesting}_i - \text{Leaching}_i \quad (1)$$

where Δ =net accumulation (+) or net loss. A net change in the base cation pool is the change in the pool of exchangeable cations in soil and, in case of increasing or decreasing humus layer thickness, the change in the pool of base cations bound to soil organic matter. All budget terms were assumed to be constant in the calculations. Whereas current rates, or approximations of current rates, can be used for the deposition, weathering and leaching terms, the harvesting term must be regarded in the perspective of a whole forest rotation. Thus, the results of the calculations give the yearly net change as an average for a forest rotation, provided that the other terms are constant over time.

Mapping was performed on the entire forested area of Sweden, viz. 23 10⁶ hectares ranging from 55 to 69°N. The transition from temperate to boreal climate is at about 60°N. The coniferous species Norway spruce (*Picea abies* (L.) H. Karst.) and Scots pine (*Pinus sylvestris* L.) are dominant, birch being the

most common deciduous species (*Betula pubescens* Ehrh. and *Betula pendula* Roth). The dominant method of regeneration felling is clearcutting. The calculations are not valid for ditched organic forest soils, i.e., 7% of the managed forest area, since no data were available for such conditions.

Mass balance calculations were performed on a GIS platform with a resolution of 5.5 km. The calculations were based on a geographical database containing base cation deposition data and the parameters needed to estimate base cation weathering, leaching and loss through harvesting. Rates were interpolated by kriging to the 5.5 km grid. The effects of future harvesting policies on the base cation budget were assessed by using scenarios. The data acquisition of deposition, weathering rates, harvest losses and leaching are described briefly below and more thoroughly in Akselsson (2005).

2.1 Data Acquisition

2.1.1 Deposition

Base cation deposition for 1998 modelled in a 5.5 km grid with the dispersion model MATCH (Langner, Persson, Robertson, & Ullerstig, 1996), provided the framework and resolution of the calculations.

2.1.2 Weathering Rates

Base cation weathering rates were modelled using the steady-state soil chemistry model PROFILE (Sverdrup & Warfvinge, 1993). Soil properties, such as mineral composition, soil moisture, particle-specific surface area, pH, cation and organic acid concentrations and temperature, are required for the PROFILE calculations. The basis for the modelling was elemental analyses (total concentrations) of soil on a total of 243,63 sites (Akselsson, 2005), supplied by the Swedish Geological Survey (SGU) (Lax & Selinus, 2005), the National Forest Inventory (Hägglund, 1985) and the Swedish mining company Terra Mining. The results from the elemental analyses were transformed into mineralogical composition using a normative model (Akselsson et al., 2004; SAEFL, 1998). The sites were then assigned data for all the required input parameters from the best available source, i.e., different national databases, as described in Akselsson et al. (2004). Boulders, cobbles and

pebbles decrease the amount of weatherable soil and thus the weathering rate per hectare. To compensate for the amount of coarse-grained material (here defined as grain sizes >20 mm, i.e., boulders, cobbles and large pebbles), a constant fraction of 30% was assumed for all soils, based on soil texture distribution curves from ten sites on sandy glacial tills (T. Pässe, pers. comm.). Weathering was modelled to different depths for spruce (40 cm) and pine (50 cm), due to their different root depths, based on data in Rosengren and Stjernquist (2004). The resulting Ca, Mg and K weathering rates on the sites were interpolated by kriging to the 5.5 km grid according to Akselsson (2005).

2.1.3 Harvesting

The base cation losses in harvested stems, branches and needles were estimated by multiplying net growth rates in the 5.5 km grid, interpolated from data from the Swedish National Forest Inventory (Hägglund, 1985), by the base cation concentration in the different tree parts of the different tree species (Jacobson & Mattson, 1998; Egnell, Nohrstedt, Weslien, Westling, & Örlander, 1998). The harvesting was thus assumed to be equal to the net growth rate. Since in practice it is impossible to remove all branches and needles from the forest floor, another factor was introduced for the branches and needles, namely the fraction of the harvested branches and needles that was removed. This is described in Section 2.2.

2.1.4 Leaching

The base cation leaching was based on soil water analyses of suction lysimeter samples from ninety-two coniferous sites at a depth of 50 cm (Hallgren Larsson, Knulst, Malm, & Westling, 1995), combined with runoff data from the Swedish Meteorological and Hydrological Institute (SMHI) (Raab & Vedin, 1995). The concentrations were assumed to be the same in pine forests as in spruce forests and the runoff data was not forest species specific. Thus no differentiation was made between leaching in spruce and pine forests. Medians from the soil water measurements from the three years 2001–2003, with three measurements per year, were used. The geostatistical analysis showed spatial autocorrelation for all base cations, although it was rather weak. Kriging interpolation of

the concentrations was performed to the 5.5 km grid. The leaching for each 5.5 km grid cell was calculated by multiplying the interpolated concentrations by the runoff volume.

2.2 Scenario Assessments

Two different harvesting intensity scenarios were investigated for spruce and pine separately: a stem harvesting scenario and a whole-tree harvesting scenario. Stem harvesting was defined as removal of the stem only, whereas whole-tree harvesting was defined as harvesting of the stem together with 75% of the branches in thinning and in final felling. Furthermore, it was assumed that 75% of the needles was removed with the branches. The fraction for branches was based on an “intensive harvest” scenario from the National Board of Forestry, and the fraction for needles was based on a study of needle loss in slash removal (S. Jacobson, pers. comm.).

2.3 Comparisons of Budgets with Pools of Base Cations in Spruce Forests

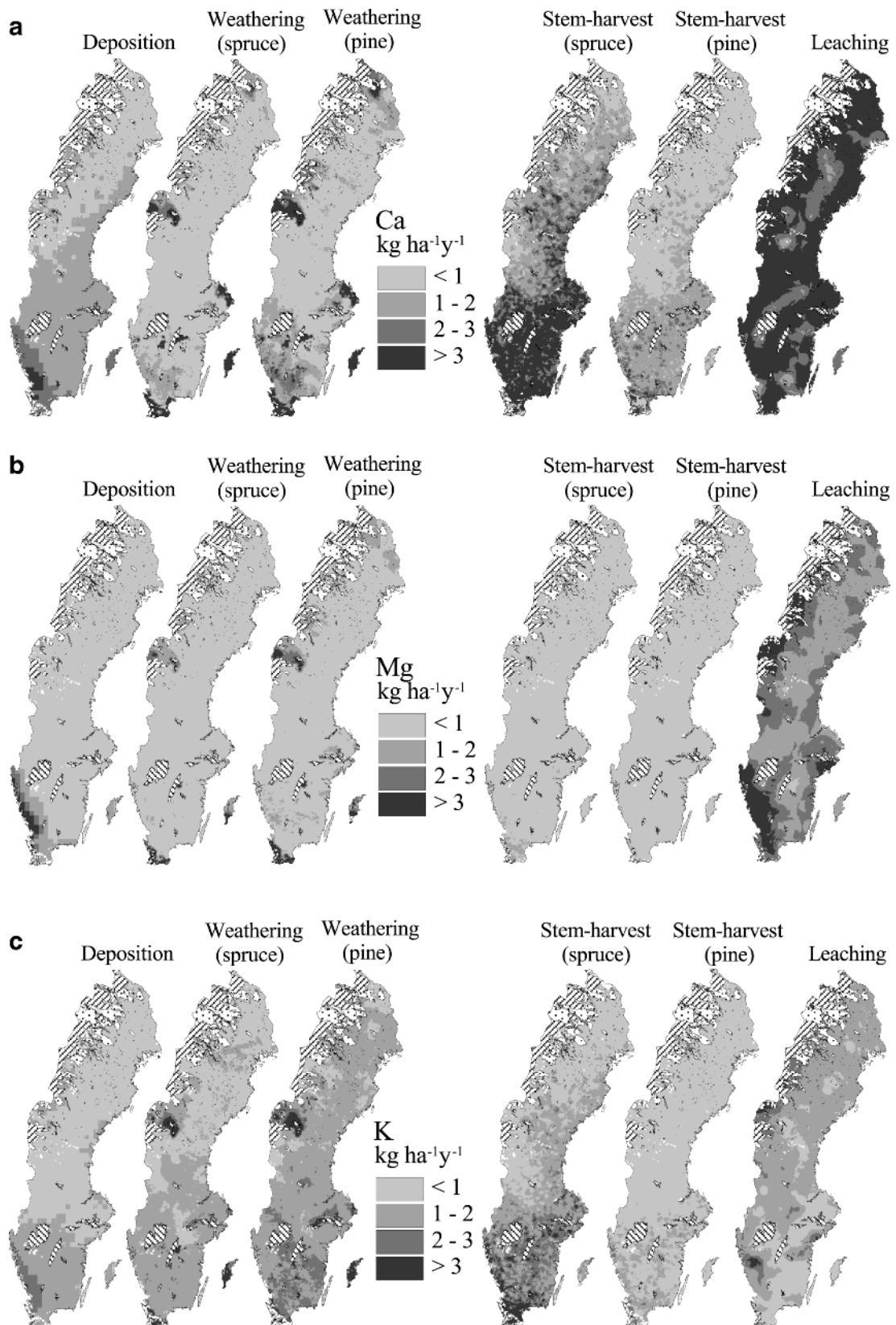
The pool of exchangeable base cations to a depth of 40 cm (including the organic layer), corresponding to the employed root depth in spruce forests, was approximated based on 622 spruce sites (defined as sites with at least 50% spruce) from the National Forest Inventory (data from the 1990s). The amounts of exchangeable base cations have been analysed by extraction with ammonium acetate. Soil densities from a study by Karlun (1995) were used and a constant fraction of coarse-grained material (grain sizes >20 mm) of 30% was assumed in accordance with the weathering calculations.

2.4 Regionalized Mass Balance Terms

The mass balance terms, regionalized in accordance with the descriptions above, are presented in Fig. 1.

3 Results

The nutrient balance for Ca was negative for most parts of Sweden in all four cases (Fig. 2). Most parts of the country showed net losses of up to $4 \text{ kg ha}^{-1} \text{ y}^{-1}$ in pine forests and the losses were greater in the whole-tree



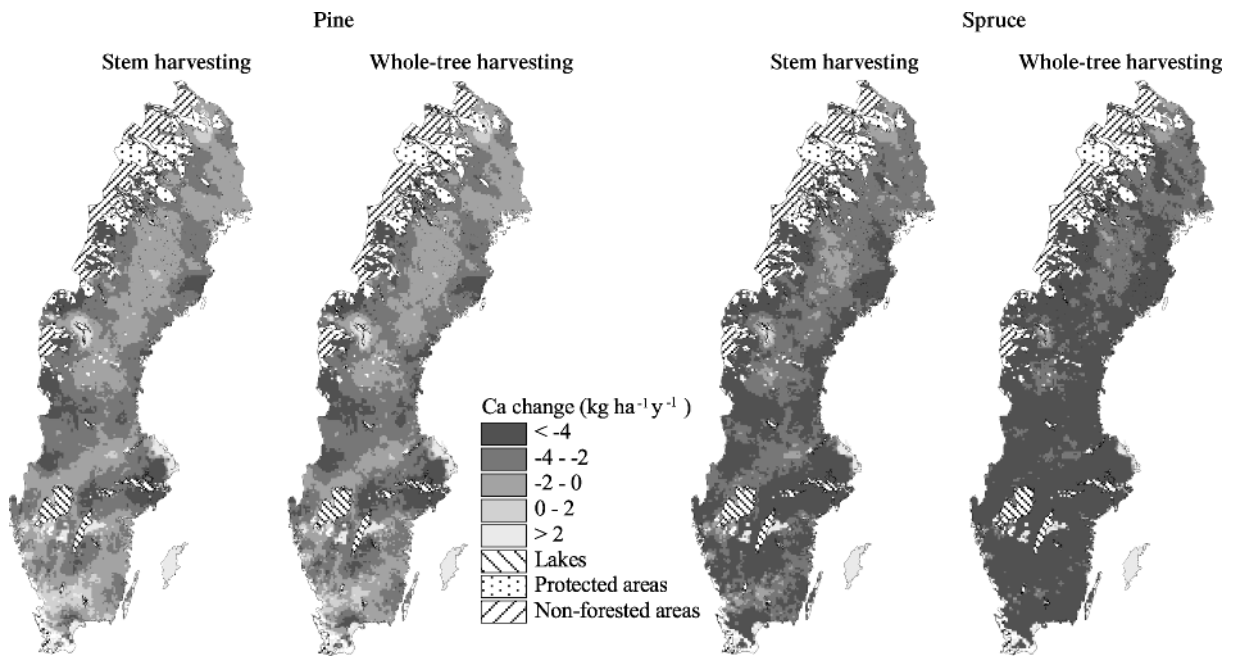


Fig. 2 Results of Ca budget calculations for the four different cases

harvesting scenario than in the stem harvesting scenario. In the spruce forests net losses of more than $4 \text{ kg ha}^{-1} \text{ y}^{-1}$ were common, especially in the whole-tree harvesting scenario. The effect of harvesting on the Ca budget is also shown in Table 1, where the calculated budget results in spruce forests with whole-tree harvesting, stem harvesting and without harvesting are compared. In the whole-tree harvesting scenario 95% of the forest area showed net losses of more than $2 \text{ kg ha}^{-1} \text{ y}^{-1}$ and 74% showed net losses of more than $4 \text{ kg ha}^{-1} \text{ y}^{-1}$. In the stem harvesting scenario the corresponding figures were 85% and 45%. When harvesting was not included the areas with net losses of more than $2 \text{ kg ha}^{-1} \text{ y}^{-1}$ were smaller, 38%, and only 9% of the forest area showed net losses of more than $4 \text{ kg ha}^{-1} \text{ y}^{-1}$.

Also for Mg the balances were negative in most parts of the country (Fig. 3). The difference between the pine and spruce forests and the effect of harvesting was not as large as for Ca (Fig. 3, Table 2). Losses

of up to $2 \text{ kg ha}^{-1} \text{ y}^{-1}$ were most common. The frequency of grid cells with losses greater than this was the highest in the case of spruce forests and whole-tree harvesting.

For K, positive balances dominated in the pine forests, while the opposite was found in the spruce forests (Fig. 4). Whole-tree harvesting increased the net losses substantially in the spruce forests. The budget if harvesting was excluded in the calculations showed negative budgets on only 13% of the area (Table 3). The budget maps showed no clear geographical gradients.

Table 1 Area fraction (%) of different Δ classes for the Ca budget in spruce forests without harvesting ($\Delta = \text{Deposition} + \text{Weathering} - \text{Leaching}$) and with stem- and whole-tree harvesting ($\Delta = \text{Deposition} + \text{Weathering} - \text{Leaching} - \text{Harvesting}$)

$\Delta \text{ Ca (kg ha}^{-1} \text{ y}^{-1})$	Area fraction (%)		
	Harvesting excluded	Stem harvesting	Whole-tree harvesting
<-4	9.1	44.9	73.6
-4--2	28.9	40.6	21.1
-2--0	45.9	11.3	2.7
0--2	11.5	0.7	0.4
>2	4.6	2.5	2.1

Fig. 1 Deposition, weathering, harvesting (stem harvesting scenario) and leaching of Ca (a), Mg (b) and K (c). The calculated weathering and harvesting differs between spruce and pine forests, whereas the same deposition and leaching is used for both spruce and pine forests. Dashed and dotted areas are lakes, non-forested areas and protected areas not included in the mapping

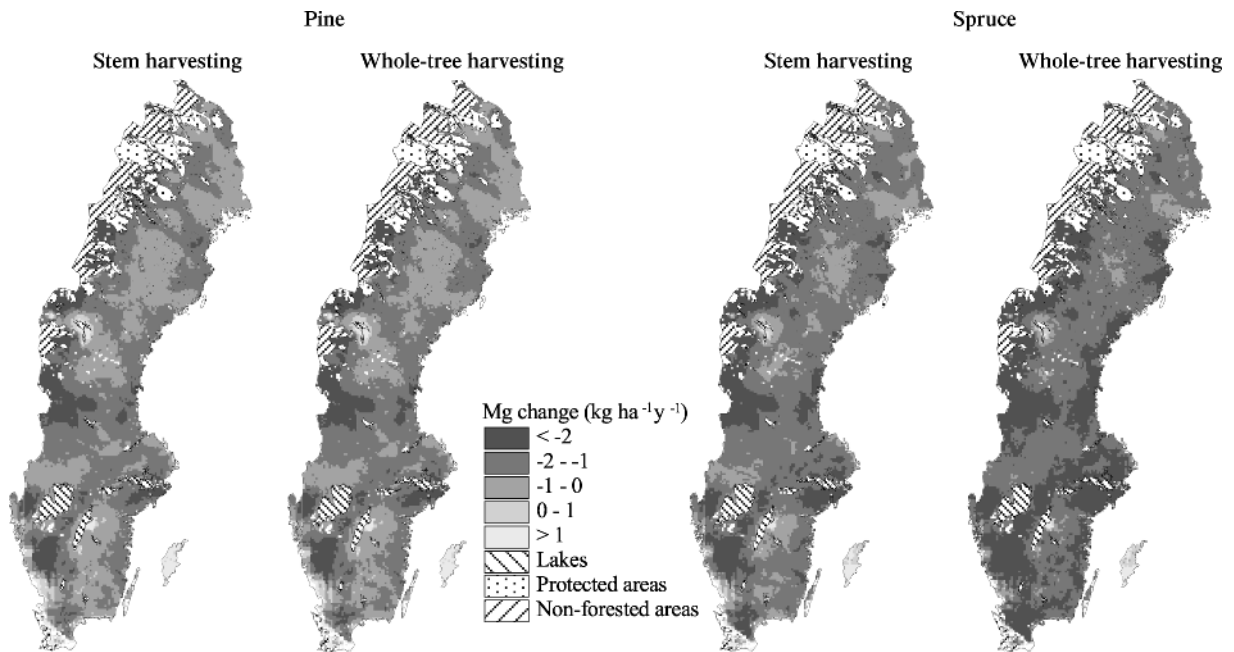


Fig. 3 Results of Mg budget calculations for the four different cases

The pools of exchangeable base cations at 622 spruce sites, here defined as sites with at least 50% spruce, showed a substantial local variation, but some regional patterns could be found (Fig. 5). As can be seen in Fig. 5 the proportion of sites with large pools of base cations was high in the eastern part of southern-central Sweden, where the pools on most sites were over 700 kg ha^{-1} for Ca, over 80 kg ha^{-1} for Mg and over 200 kg ha^{-1} for K. The proportion of sites with small pools of Ca was high in the southwestern parts of Sweden, where the pool was smaller than 300 kg ha^{-1} on almost all sites. At 25%

of the analysed sites the yearly net losses of Ca, K and Mg constituted at least 3, 6 and 1%, respectively, of the pool of exchangeable base cations for stem harvesting of spruce (Table 4). In the whole-tree harvesting scenario the corresponding figures were 6, 7 and 4%. However, since the frequency of sites differs in different parts of Sweden, and since the fraction of spruce forests varies geographically, these figures are not representative for Swedish spruce forests in general, but only for the 622 spruce sites.

4 Discussion

The results from the budget calculations indicate that there is a risk of nutrient deficiency within one forest rotation in parts of Sweden, especially if whole-tree harvesting is employed. This suggests that compensatory fertilization is required to avoid net losses. The higher harvesting losses from spruce forests than from pine forests are due to the higher growth rates and higher concentrations of base cations in spruce. Moreover, the amount of weathered base cations available was substantially higher in the pine forests (Fig. 1), due to their deeper root systems. The effect of whole-tree harvesting was most obvious in the spruce forests, since the amount of branches and

Table 2 Area fraction (%) of different Δ classes for the Mg budget in spruce forests without harvesting ($\Delta = \text{Deposition} + \text{Weathering} - \text{Leaching}$) and with stem- and whole-tree harvesting ($\Delta = \text{Deposition} + \text{Weathering} - \text{Leaching} - \text{Harvesting}$)

$\Delta \text{ Mg (kg ha}^{-1} \text{ y}^{-1})$	Area fraction (%)		
	Harvesting excluded	Stem harvesting	Whole-tree harvesting
<-4	14.7	23.9	41.2
-4--2	44.7	56.6	51.2
-2-0	36.2	16.9	5.8
0-2	2.6	1.2	1.0
>2	1.7	1.3	0.9

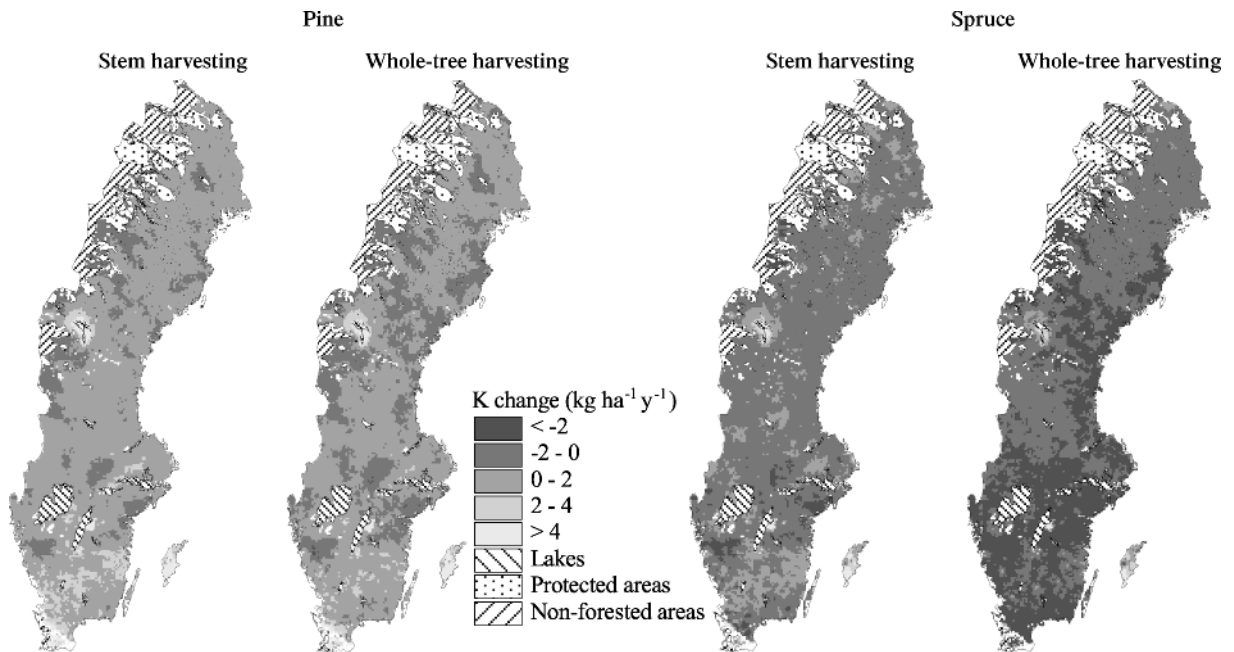


Fig. 4 Results of K budget calculations for the four different cases

needles is substantially larger in a spruce forest than in a pine forest. Furthermore, the effect of whole-tree harvesting in the spruce forests was most obvious for K, since K is the base cation for which the harvesting term has the greatest relative importance in the budget. The harvesting intensity also had a substantial effect on the Ca budget. For Mg the leaching term dominated completely and the harvesting intensity was of minor importance (Fig. 1b). The high biomass concentrations of K and Ca, compared to Mg, depend on a relatively higher plant demand for K and a higher luxury uptake of Ca, respectively. The inputs were

generally higher in the southern parts of Sweden, but this was counteracted by the higher harvesting losses and also, to some extent, relatively high leaching losses in southern regions.

The fact that the Ca and Mg budgets were negative even if harvesting was not included in the calculations indicates that the leaching is enhanced due to acidification (Haynes & Swift, 1986). Decreased acid deposition results in decreased base cation leaching, as shown by Moldan et al. (2004), but the recovery process is slowed down by sulphate adsorption (Martinson, 2004). Thus the base cation leaching can be expected to decrease in the future. However, it is difficult to quantify the impact of acidification on the base cation budgets since small net changes involve uncertainties mainly due to limitations in input data, especially concerning leaching.

Two regional studies of base cation budgets have been carried out previously in Sweden. Sverdrup and Rosén (1998) used basically the same concept as in the present study to calculate base cation budgets in Sweden. The main improvements in the present study is that the input data has been greatly improved and has a higher resolution, the harvesting scenarios have been updated and spruce and pine have been considered separately. The general geographical pattern and the levels of net losses in the two studies

Table 3 Area fraction (%) of different Δ classes for the K budget in spruce forests without harvesting (Δ = Deposition + Weathering – Leaching) and with stem- and whole-tree harvesting (Δ = Deposition + Weathering – Leaching – Harvesting)

Δ K (kg ha ⁻¹ y ⁻¹)	Area fraction (%)		
	Harvesting excluded	Stem harvesting	Whole-tree harvesting
<-2	0.4	3.7	40.3
-2-0	12.3	76.2	55.8
0-2	74.4	18.1	2.6
2-4	11.0	0.8	0.6
>4	2.0	1.2	0.7

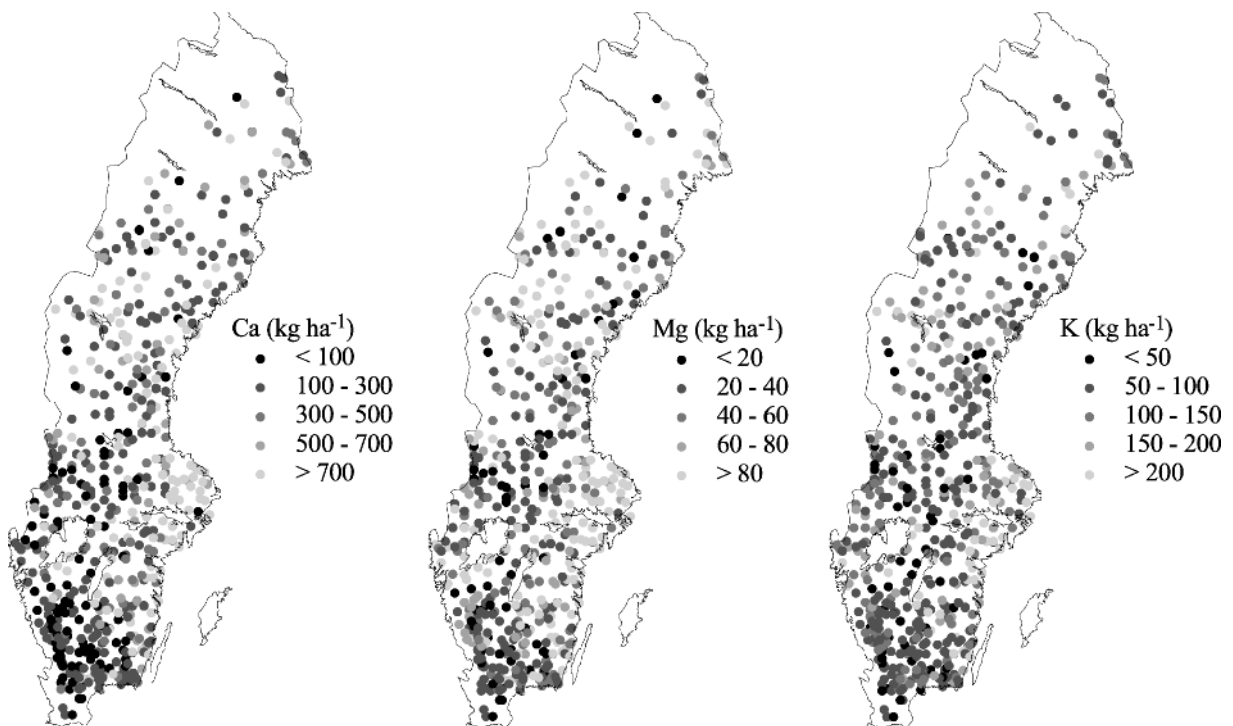


Fig. 5 Estimated amounts of exchangeable Ca, Mg and K down to a depth of 40 cm (organic layer included) on 622 spruce sites (here defined as sites with at least 50% spruce) in

the National Forest Inventory. The amounts of exchangeable base cations were analysed by extraction with ammonium acetate

were of the same order of magnitude and the two studies led to similar conclusions. Olsson et al. (1993) compared historical weathering rates with harvesting on a regional scale and concluded that weathering could not supply the Ca lost by harvesting, but that it could for Mg and K for stem harvesting, assuming a variable weathering depth from north to south. They also found that the balances were negative for Mg and K in large parts of Sweden with whole-tree harvest-

ing. Furthermore, they concluded that the net losses would increase if deposition and leaching were included, since the leaching of base cations often exceeds the deposition. This conclusion is in accordance with the results from the present study. Data from the National Forest Inventory show, on the other hand, no significant difference in the base saturation between the inventory in the 1980s and the inventory ten years later in the 1990s (Bertills, 2003), but the

Table 4 Yearly change as a fraction of pool size (%) for Ca, Mg and K in spruce forests in the stem harvesting and whole-tree harvesting scenarios on the 622 spruce sites in the National Forest Inventory

	Ca change (%)		Mg change (%)		K change (%)	
	Stem	Whole-tree	Stem	Whole-tree	Stem	Whole-tree
25-percentile	-3.4	-5.8	-5.6	-7.4	-1.0	-4.1
Median	-1.5	-2.5	-2.9	-4.0	-0.4	-2.3
75-percentile	-0.6	-1.1	-1.3	-1.8	-0.03	-1.2

Notice that the frequency of sites differs in different parts of Sweden, thus the figures are not representative for Swedish spruce forests in general, but only for the 622 spruce sites.

short time span between the inventories and the fact that the soil sampling was not performed at the same exact sites in the two different inventories mean that changes are difficult to detect.

Joki-Heiskala et al. (2003) compared historical weathering rates, in the uppermost 50 cm of the mineral soil, with harvesting in Finland and concluded that weathering could not replace K losses with stem harvesting for large parts of Finland. It could, however, replace the losses of Ca and Mg in most parts of the country. In the Swedish studies the situation was the opposite, with large losses of Ca and Mg and budgets around 0 or with small losses for K. This may be due to differences in soil mineralogical composition. Watmough and Dillon (2001) concluded, based on a monitoring study in a coniferous catchment in Ontario, Canada, that the long-term sustainability would be threatened if losses of that size were to continue.

Net losses for most parts of the country for all base cations and cases, except for the K budget in the pine forests, mean that the pool of exchangeable base cations is decreasing. The current growth of the organic layer, which has been observed in the National Forest Inventory (Jernbäcker, 2003), indicate that the net losses from the mineral soil may be somewhat higher than the estimates. The fraction of base cations of the total cation flux decreases together with the decrease in the soil pool of exchangeable base cations. The depletion of the base cation pools will thus have long-term negative effects both on the resistance to acidification of the soil and on the runoff water quality. A decrease in Ca, Mg or K availability in the soil solution will limit the uptake which could lead to reduced growth and negative effects on tree vitality on the long-term (Rosengren-Brinck, Nihlgård, Bengtsson, & Thelin, 1998).

Further work is required to reduce the uncertainties in the budget calculations. Of highest priority is the leaching term, which is assumed to contribute most to the uncertainties since the runoff data applied represent all existing land use classes, and may thus be overestimated for forests. The deposition term also involves substantial uncertainties and is thus of high priority. The uncertainties are discussed further in Akselsson (2005). Dynamic models should preferably be used as a complement to budget calculations in order to improve the possibilities to make future extrapolations.

5 Conclusions

The results indicate that the present pools of exchangeable base cations will decrease even when stem-harvesting is employed, and that the losses of Ca and K will increase substantially with whole-tree harvesting in large parts of Sweden, especially in spruce forests. The results suggest that the stores will be depleted at rates that could lead to negative effects on trees and runoff water quality within one forest rotation. The conclusions are similar to those from those presented in other studies in Sweden. Further work is required to reduce the uncertainties and thus increase the usefulness of the method in decision-making. The leaching term is of the highest priority.

Acknowledgements This study is the result of cooperation between two Swedish research programs, ASTA and SUFOR. The ASTA program is funded by MISTRA (the Foundation for Strategic Environmental Research), the Swedish Energy Agency, the National Board of Forestry in Sweden and the Swedish Environmental Protection Agency. The SUFOR program (Sustainable Forestry in Southern Sweden) is funded by MISTRA. The forest data were made available by the Swedish National Survey of Forest Soils and Vegetation, performed by the Department of Forest Soils, Swedish University of Agricultural Sciences (SLU), Uppsala. The authors are solely responsible for the interpretation of data.

References

- Akselsson, C. (2005). Regional nutrient budgets in forest soils in a policy perspective. Ph. D. Thesis, Department of Chemical Engineering, Lund University, 212 pp.
- Akselsson, C., Holmqvist, J., Alveteg, M., Kurz, D., & Sverdrup, H. (2004). Scaling and mapping regional calculations of soil chemical weathering rates in Sweden. *Water, Air, and Soil Pollution: Focus*, 4, 671–681.
- Bertills, U. (2003). Bara naturlig försurning – Underlagsrapport till fördjupad utvärdering av miljömålsarbetet. Report 5317, The Swedish Environmental Protection Agency, Stockholm, 147 pp. (In Swedish).
- Egnell, G., Nohrstedt, H.-Ö., Weslien, J., Westling, O., & Örlander, G. (1998). Miljökonsekvensbeskrivning av skogsbränsleuttag, asktillförsel och övrig näringskompensation. Report 1:1998, National Board of Forestry in Sweden, Jönköping, 170 pp. (In Swedish).
- Hägglund, B. (1985). En ny svensk riksskogstaxering (A new Swedish National Forest Survey). Report 37, Swedish University of Agricultural Sciences, Uppsala, 93 pp. (In Swedish with English summary).
- Hallgren Larsson, E., Knulst, J., Malm, G., & Westling, O. (1995). Deposition of acidifying compounds in Sweden. *Water, Air, and Soil Pollution*, 85, 2271–2276.

- Haynes, R. J., & Swift, R. S. (1986). Effects of soil acidification and subsequent leaching on levels of extractable nutrients in a soil. *Plant and Soil*, 95, 327–336.
- Jacobson, S., & Mattson, S. (1998). "Snurran" – an Excel program for calculating site nutrient levels in logging residues. Report No.1, The Forestry Research Institute of Sweden, Uppsala, 4 pp. (In Swedish with English summary).
- Jernbäcker, E. (2003). Begränsad klimatpåverkan. Underlagsrapport till fördjupad utvärdering av miljömålsarbete. Report 5316, The Swedish Environmental Protection Agency, Stockholm, 123 pp. (In Swedish).
- Joki-Heiskala, P., Johansson, M., Holmberg, M., Mattsson, T., Forsius, M., Kortelainen, P., et al. (2003). Long-term base cation balances of forest mineral soils in Finland. *Water, Air, and Soil Pollution*, 150, 255–273.
- Karltun, E. (1995). Acidification of forest soils on glacial till in Sweden – Soil chemical status and acidification processes in relation to environmental conditions. Report 4427, Swedish Environmental Protection Agency, Stockholm, 76 pp.
- Langner, J., Persson, C., Robertson, L., & Ullerstig, A. (1996). Air Pollution Assessment Study Using the MATCH Modelling System. Application to sulphur and nitrogen compounds over Sweden 1994. Report no. 69, Swedish Meteorological and Hydrological Institute, Norrköping, 38 pp.
- Lax, K., & Selinus, O. (2005). Geochemical mapping at the Geological Survey of Sweden. *Geochemistry: Exploration, Environment, Analysis*, 5, 337–346.
- Martinson, L. (2004). Recovery from acidification – Policy oriented dynamic modeling. Ph. D. Thesis, Department of Chemical Engineering, Lund University, 146 pp.
- Moldan, F., Skeffington, R. A., Mörth, C.-M., Torssander, P., Hultberg, H., & Munthe, J. (2004). Results from the covered catchment experiment at Gårdsjön, Sweden, after ten years of clean precipitation treatment. *Water, Air, and Soil Pollution*, 154, 371–384.
- Olsson, M., Rosén, K., & Melkerud, P.-A. (1993). Regional modelling of base cation losses from Swedish forest soils due to whole-tree harvesting. *Applied Geochemistry*, 2, 189–194.
- Raab, B., & Vedin, H. (1995). Klimat, sjöar och vattendrag. SNA Förlag, Stockholm, 176 pp. (In Swedish).
- Rosengren, U., & Stjernqvist, I. (2004). Gå på djupet! Om rotdjup och rotproduktion i olika skogstyper. Rahms i Lund, Sweden, 55 pp. (In Swedish).
- Rosengren-Brinck, U., Nihlgård, B., Bengtsson, M., Thelin, G. (1998). Samband mellan barrförlust, barrkemi och markkemi i Skåne. In U. Rosengren-Brinck (Ed.), *Needle loss and air pollution : relationships between crown defoliation and site factors in Swedish forest*, Report 4890 (120 pp.). Stockholm: Swedish Environmental Protection Agency, (In Swedish).
- SAEFL (1998). Critical loads of acidity for forest soils. Environmental Documentation No. 88, Air/Forest, Swiss Agency for the Environment, Forest and Landscape, Bern, 102 pp.
- Sverdrup, H., & Rosén, K. (1998). Long-term base cation mass balances for Swedish forests and the concept of sustainability. *Forest Ecology and Management*, 110, 221–236.
- Sverdrup, H., & Warfvinge, P. (1993). Calculating field weathering rates using a mechanistic geochemical model (PRO-FILE). *Journal of Applied Geochemistry*, 8, 273–283.
- Watmough, S. A., & Dillon, P. J. (2001). Base cation losses from a coniferous catchment in central Ontario, Canada. *Water, Air, and Soil Pollution: Focus*, 1, 507–524.

Long Term Effects of Acid Irrigation at the Höglwald on Seepage Water Chemistry and Nutrient Cycling

Wendelin Weis · Roland Baier · Christian Huber · Axel Göttlein

Received: 13 June 2005 / Accepted: 14 August 2006 / Published online: 13 March 2007
© Springer Science + Business Media B.V. 2007

Abstract In order to test the hypothesis of aluminium toxicity induced by acid deposition, an experimental acid irrigation was carried out in a mature Norway spruce stand in Southern Germany (Höglwald). The experiment comprised three plots: no irrigation, irrigation (170 mm a^{-1}), and acid irrigation with diluted sulphuric acid (pH of 2.6–2.8). During the seven years of acid irrigation (1984–1990) water containing $0.43 \text{ mol}_e \text{ m}^{-2} \text{ a}^{-1}$ of protons and sulphate was added with a mean pH of 3.2 (throughfall+acid irrigation water) compared to 4.9 (throughfall) on both control plots. Most of the additional proton input was consumed in the organic layer and the upper mineral soil. Acid irrigation resulted in a long lasting elevation of sulphate concentrations in the seepage water. Together with sulphate both aluminium and appreciable amounts of base cations were leached from the main rooting zone. The ratio between base cations (Ca+Mg+K) and aluminium was 0.79 during acid irrigation and 0.92 on the control. Neither tree growth and nutrition nor the pool of exchangeable cations were affected significantly. We conclude that at this site

protection mechanisms against aluminium toxicity exist and that additional base cation runoff can still be compensated without further reduction of the supply of exchangeable base cations in the upper mineral soil.

Keywords Acid deposition · Aluminium · Base cations · Norway spruce · Soil acidification · Sulphate

1 Introduction

Acid rain is a problem of the industrialised world. Emissions of SO_2 and NO_x from combustion processes react with water and are deposited as sulphuric and nitric acid. Since the 1970s acid deposition is considered to cause ecologically relevant changes in the soil and to accelerate soil acidification. Losses of nutrient cations and an increased release of phytotoxic aluminium species and of heavy metals are possible causes for forest decline (Nair and Prenzel 1978; Reuss and Johnson 1986; Ulrich 1983a; van Breemen et al. 1983). In order to test the hypothesis of aluminium toxicity induced by acid deposition in the field, an experimental acid irrigation was carried out in a mature Norway spruce stand in Southern Germany. The tree species was decided on as it is both acidophilous and economically important. A site

W. Weis (✉) · R. Baier · C. Huber · A. Göttlein
Fachgebiet Waldernährung und Wasserhaushalt,
Technische Universität München,
Am Hochanger 13,
85354 Freising, Germany
e-mail: weisw@forst.tu-muenchen.de

with non-limiting water and nutrient supply was selected in order to be able to distinguish between enhanced nutrient cation losses and an actually toxic effect on tree growth due to high proton and aluminium concentrations in the soil (Kreutzer and Weiss 1998). Since the beginning of the investigations in 1984 a huge data set has been collected allowing us to balance nutrient fluxes under normal conditions and under the influence of an experimentally elevated acid deposition. As in other long-lasting ecological studies statistical analyses of the data is almost impossible. However, the many different and coordinated investigations carried out on the same plots and the long-lasting investigation period of more than 20 years represent a special value with the possibility to include the results from this site in recommendations for forest and land-use planning and management. Explicitly we want to answer the following questions:

1. Did the experimental acid irrigation at Höglwald lead to a reduction of pH in soil and seepage water with negative effects on root system and tree growth?
2. Did the buffering of the deposited protons in the soil lead to ratios between base cations and aluminium unfavourable for tree growth?
3. Will the additionally deposited sulphate as a mobile anion lead to surplus losses of base cation nutrients from the main rooting zone and if yes, is this nutrient depletion already visible in the pool of exchangeable cations?

2 Materials and Methods

Between 1984 and 1990 an acid irrigation experiment was carried out at a forest district 50 km west of Munich at an elevation of 540 m. The “Höglwald” is a well growing Norway spruce stand planted around 1910. The soil is a Dystric Cambisol derived from Pleistocene Loess over Tertiary silty sand and covered by 5 cm of a typical moder. Basic data on soil chemistry is given in Table 1. The mineral soil up to the depth of 40 cm is strongly acidified with a base saturation of less than 10%. If following the classification of buffer ranges given in Ulrich (1983a), it belongs to the aluminium buffer range (pH 4.2 to 2.8). Below 40 cm depth the soil falls into the cation exchange buffer range (pH 5.0 to 4.2). The mean annual temperature is 7.8°C and the annual precipitation 870 mm. Nitrogen input amounts to some 30 kg ha⁻¹ a⁻¹. Sulphur input decreased from 24 kg ha⁻¹ a⁻¹ in 1984 to 7 kg ha⁻¹ a⁻¹ in 2003. The pH measured in bulk precipitation and throughfall averages 4.9 and 5.2, respectively.

The experiment comprised three adjacent plots with an area of 2,500 m² each: One control without irrigation, one plot irrigated with water similar in chemical composition to bulk precipitation and one plot irrigated with the same water adjusted to a pH of 2.6–2.8 by the addition of sulphuric acid. On 14–16 occasions between May and October/November 1984 through 1990, a sprinkler system distributed some 11 mm irrigation water on the plots. The acid

Table 1 Basic soil chemical parameters for the Norway spruce stand at Höglwald

Horizon	pH (H ₂ O)	CEC [mmol _c kg ⁻¹]	BS [%]	C _{org} [%]	N _{tot} [%]	C/N
L	4.67	205	81	45.50	1.67	27
Of1	4.01	209	75			
Of2	3.65	206	62	43.94	1.79	25
Oh	3.51	191	40	34.54	1.15	30
0–5 cm	3.75	85	10	5.05	0.27	19
5–10 cm	3.94	62	6	1.91	0.10	19
10–20 cm	4.12	46	6	0.92	0.06	15
20–30 cm	4.19	44	6	0.42	0.03	14
30–40 cm	4.15	57	6	0.20	0.02	10
40–60 cm	4.33	98	24	0.11	0.01	11
60–80 cm	4.55	113	49	0.11	0.01	11

The values are means of sampling between 1984 and 1995 on the control plot (Kreutzer and Weiss 1998, modified, CEC: cation exchange capacity; BS: base saturation; C_{org}: organic carbon; N_{tot}: total nitrogen)

irrigation resulted in an additional input of $0.43 \text{ mol}_e \text{ m}^{-2} \text{ a}^{-1}$ of protons and sulphate. The annual input of sulphate in throughfall, the additional input with acid irrigation and the development of the SO_2 emissions in West Germany are shown in Fig. 1.

Bulk precipitation (three replicates), throughfall (12 replicates) and the outflow from the organic layer (gravitation lysimeters, eight replicates per plot, since 1986) were sampled every two weeks, the seepage water in 20, 40 and 175 cm soil depth (suction cup lysimeters, 5–7 replicates per plot) once a month (1984–2004). In this paper we will focus on the seepage water in 40 cm soil depth because of two reasons which are relevant for the investigation of enhanced acidification and aluminium toxicity: (1) 90% of the fine roots are located above 40 cm soil depth (see below), and (2) above 40 cm soil depth, the base saturation is below 10% but increases thereafter. The water samples were analysed for pH, the concentrations of chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) (ion chromatograph, Dionex), and the cations ammonium (NH_4^+) (auto analyser, SKALAR analytic GmbH), aluminium (Al^{3+}), iron (Fe^{3+}), manganese (Mn^{2+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+) (ICO-OES, Perkin Elmer). Cation exchange capacity was measured by extraction with 1 M NH_4Cl in 1991 and 2004. For further information on the experimentation site and experimental details see Kreutzer et al. (1991) and Kreutzer and Weiss (1998).

Mean annual net nutrient uptake of the spruce trees was calculated from the mean annual increment (analyses of the tree rings between 1979 and 1998) of stem wood and bark and the respective element content, which had been obtained after a biomass investigation in 1998 (Table 2). As the trees are more

than 90 years old and the last thinning happened in 1975, 10 years before the beginning of the experiment, we neglected nutrient uptake due to canopy growth.

The element fluxes were calculated by multiplying the arithmetic mean of the element concentration of every sampling date with the sum of the modelled water fluxes between this date and its predecessor. To obtain flux weighted mean annual element concentrations, we divided the annual element fluxes by the respective water fluxes. We calculated annual base cation leaching from the main rooting zone using element fluxes in throughfall including irrigation and in the seepage water in 40 cm soil depth. Presuming that marine influence at Höglwald is low, that sodium is an inert tracer, and that the size of aerosols is similar for all base cations, canopy leaching was excluded using the ratio of sodium in bulk precipitation and throughfall (Ulrich 1983b).

The water fluxes were calculated using the mechanistic model described in Huber et al. (2004b). The input data (hourly values of bulk precipitation, air temperature, relative humidity, and wind speed) were either measured on the plot or taken from the nearest DWD (Deutscher Wetterdienst) weather station situated 16 km to the northwest. In order to simulate the experimental sub-canopy irrigation, the amount of irrigation water was added to throughfall so that it did not interfere with the calculation of interception loss from the spruce canopy. The evaporation rate was calculated from vapour pressure deficit (VPD) multiplied by a specific evaporating surface. For interception loss this surface is the leaf and bark surface wetted by rainfall, with conifer needles wetted on both sides and bark sheltered from wetting during rain events with an intensity of less than 5 mm h^{-1} . The

Fig. 1 Annual sulphur input with throughfall and acid irrigation 1984–2003. The dotted line is the annual SO_2 emissions in West Germany as reported by the Umweltbundesamt (1997)

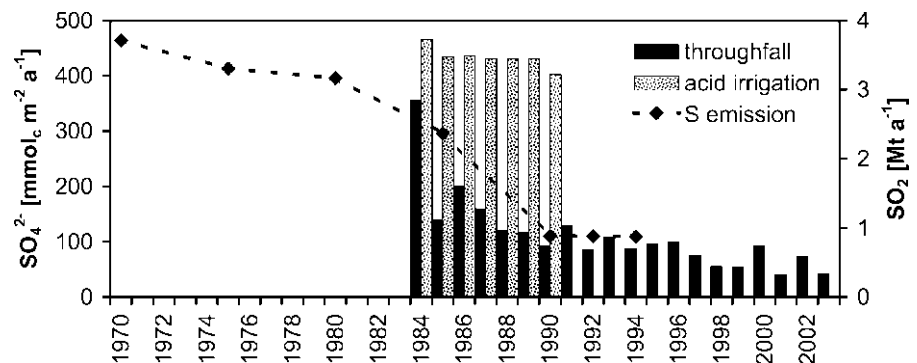


Table 2 Growing stock, increment, material density and element content in stem wood and bark of the mature Norway spruce stand in Southern Germany (Höglwald)

	Growing stock [m ³ ha ⁻¹]	Increment ^b [m ³ ha ⁻¹ a ⁻¹]	Density [kg m ⁻³]	Mean element content										
				C	N	P	Ca	Mg	K	Na	Mn	Fe	Zn	Al
				[g kg ⁻¹]										
wood ^a	1094	18.46	408	493	1.03	0.051	0.66	0.11	0.28	0.008	0.22	0.014	0.011	0.006
bark ^a	50	0.78	662	510	5.09	0.447	10.75	0.91	1.62	0.005	1.65	0.053	0.130	0.079

^a stem only^b mean of the years 1978–1998

canopy is wetted from top to down, so that during slight rain events only parts contribute to interception loss. In case of transpiration, the evaporating surface is calculated from leaf surface, the amount of stomata per leaf area and the inner surface of the sub-stomatal cavity. The latter was estimated from microscopic photographs to be about 0.00115 mm². Transpiration is only allowed between dawn and sunset calculated from the geographic latitude. Leaf and stem area indices were calculated from biomass investigations and are 6.05 and 3.48, respectively, for the Norway spruce stand at Höglwald. We used the same values for all three plots. A factor of 1.25 was used to obtain the total needle surface from the leaf area index. No soil evaporation was calculated as the soil is almost completely covered by a moss layer. The leaf surface area of the moss was estimated at 2 m² per m² soil surface. The soil water fluxes were calculated for the organic layer and five layers à 20 cm depth in the mineral soil. We used the Darcy–Richards equation to calculate the water fluxes through the soil. The relations between matrix potential, water content, and hydraulic conductivity of each soil layer were

determined in undisturbed soil cores (Ø 15 cm, height 20 cm) using a set of one TDR-probe (Trime P2, IMKO-GmbH, Ettlingen, Germany) and two tensiometers (miniature pressure-transducer tensiometer T5, UMS GmbH, Munich, Germany) installed horizontally in the core (Table 3). The soil water uptake of the spruce trees was assumed to follow the fine root distribution. Combining the results from Kreutzer et al. (1991) this distribution is as follows: 10% in the organic layer, 65% between 0 and 20 cm, 15% between 20 and 40 cm, 4% between 40 and 60 cm, 3% between 60 and 80 cm, and 3% between 80 and 100 cm. Mosses were supposed to root only in the organic layer. The reduction of transpiration during periods of low soil water contents was calculated from soil hydraulic conductivity, root potential and root density. The model was validated against measured throughfall (control plot, 10 replicates, sampled every 2 weeks, 2000 through 2003) and soil water content (control plot and acid irrigated plot) calculated from tensiometer measurements (16 replicates per plot in 10, 30 and 50 cm soil depth, 1985 through 1987) using the same pF-curves as in the

Table 3 Soil texture and the soil hydraulic parameters used to calculate soil water fluxes for the Norway spruce stand at Höglwald

Horizon	Sand	Silt	Clay	Θ _s [%]	Θ _r [%]	a [kPa ⁻¹]	b	c	R _Θ ²	k _s [mm h ⁻¹]	k _{6.3} [mm h ⁻¹]	d	R _k ²
organic layer	moder			78,1	0,0	4,054	1,33	0,25	0,98	6,710	0,0118	2,42	0,91
0–20 cm	0,40	0,33	0,27	36,9	15,8	0,349	1,16	0,14	0,99	96,451	0,0054	1,12	0,83
20–40 cm	0,36	0,33	0,32	37,1	0,0	1,933	1,04	0,04	0,90	2,215	0,0057	1,37	0,93
40–60 cm	0,24	0,51	0,25	38,1	9,8	0,176	1,12	0,11	0,99	0,882	0,0062	0,86	0,77
60–80 cm	0,17	0,66	0,17	46,0	12,7	0,074	1,23	0,19	0,98	0,507	0,0080	1,10	0,91
80–100 cm	0,16	0,65	0,19	51,3	21,3	0,078	1,56	0,36	0,99	4,110	0,0273	1,32	0,67

$$\Theta(\psi) = \Theta_r + (\Theta_s - \Theta_r) / ((1 + (-a\psi)^b)^c) \quad k(\psi) = k_{6.3} * (-\psi/6.3)^d$$

(Θ_s: water content at saturation; Θ_r: residual water content; ψ: matrix potential; k_s: hydraulic conductivity at saturation; k_{6.3}: hydraulic conductivity at -6.3 kPa)

model. The modelled throughfall values were well in the range given by the 10 replicates. Between 0 and 60 cm soil depth the bias calculated as the mean deviation of measured and modelled soil water contents relative to measured values was -0.79% for the control plot and -1.16% for the acid irrigation plot. The precision given by the standard deviation of the difference between measured and modelled relative to measured values was 3.31 and 2.29%, respectively. This resulted in an accuracy (square root of the sum between squared bias and squared precision) of 3.40 and 2.57%, which makes the model results highly acceptable.

3 Results

The additional water input during the irrigation experiment guaranteed an optimal water supply of the trees. According to the modelled water fluxes, the difference between potential and actual transpiration was less than 1% during the years of irrigation in contrast to up to 6% as calculated for the control plot. About 90% of the irrigated water left the rooting zone.

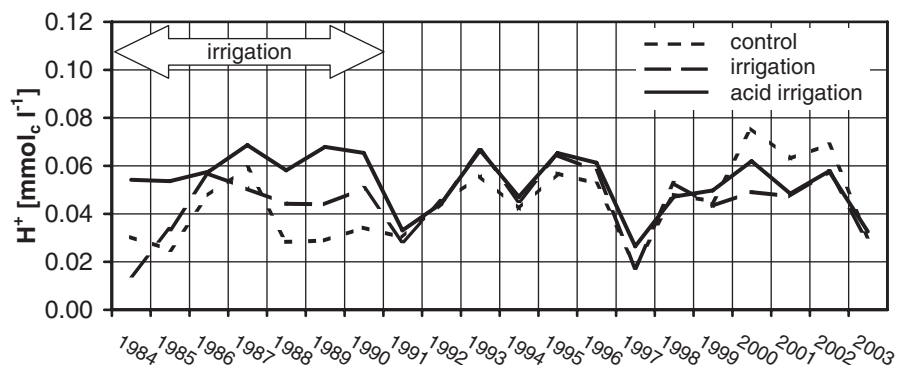
During the seven years of acid irrigation the mean pH of the water infiltrating the soil (irrigation water+ throughfall) was 3.2 compared to a pH of 4.9 on both the control and the irrigated plot. Most of the proton input during acid irrigation was consumed in the organic layer and the upper mineral soil. Between 1987 and 1990, the years with acid irrigation and available measurements of the ion concentrations in the efflux of the organic layer, we calculated an proton influx of $1.08 \text{ mol}_c \text{ m}^{-2}$ into the mineral soil

which is $0.54 \text{ mol}_c \text{ m}^{-2}$ higher than on the control plot. The difference equals only 32% of the $1.70 \text{ mol}_c \text{ m}^{-2} \text{ H}^+$ deposited with the acid irrigation water. In the seepage water in 40 cm soil depth elevated proton concentrations due to acid irrigation were restricted to the 7 years of acid irrigation and were 50% higher than on the control and non-acid irrigated plot with mean annual pH values of 4.2 and 4.4, respectively (Fig. 2). However, between 1984 and 1990 only $0.08 \text{ mol}_c \text{ m}^{-2}$ of the added $3.03 \text{ mol}_c \text{ m}^{-2}$ protons left the main rooting zone.

In the soil, acid irrigation reduced the pH-values by approximately 0.1 pH-units up to a soil depth of 40 cm. The cation exchange capacity decreased only in the uppermost horizons of the organic layer and not in the mineral soil, whereas base saturation showed little response to the additional proton input throughout the whole soil profile. Fourteen years after the end of the experimental acidification no significant differences in soil pH and cation exchange capacity on the control and acid irrigation plot were visible any longer (Fig. 3). However, from 1991 to 2004, a significant reduction of the base saturation is visible in the soil horizon between 40 and 60 cm on both the control and the acid irrigation plot indicating a progression of soil acidification with time. Non acid irrigation did not affect the soil chemical properties (data not shown).

In response to acid irrigation, the sulphate concentration in the seepage water in 40 cm soil depth was more than twice as high as on the control and non-acid irrigated plot. Elevated values were still visible in 1995, 5 years after the end of the irrigation experiment (Fig. 4). Interestingly, non-acid irrigation did not decrease the sulphate concentrations in 40 cm soil

Fig. 2 Flux-weighted annual means of the proton concentration in the seepage water in 40 cm soil depth on the control, the non-acid irrigated, and the acid-irrigated plot at Höglwald



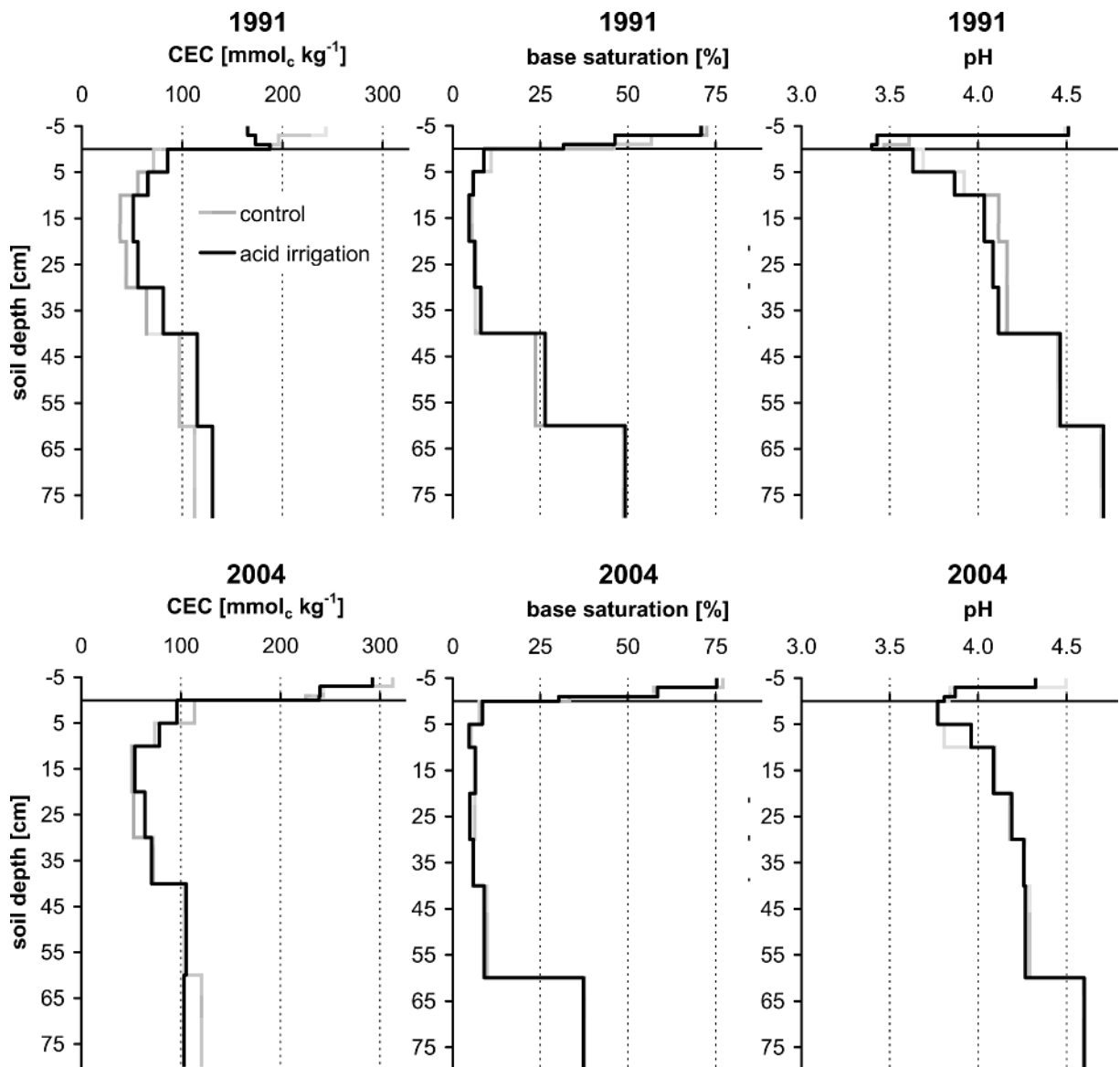


Fig. 3 Comparison of the cation exchange capacity (CEC), the base saturation, and the soil pH (H₂O) on the control and the acid irrigated plot measured in the first year after the end of the experimental irrigation (1991) and 13 years later (2004)

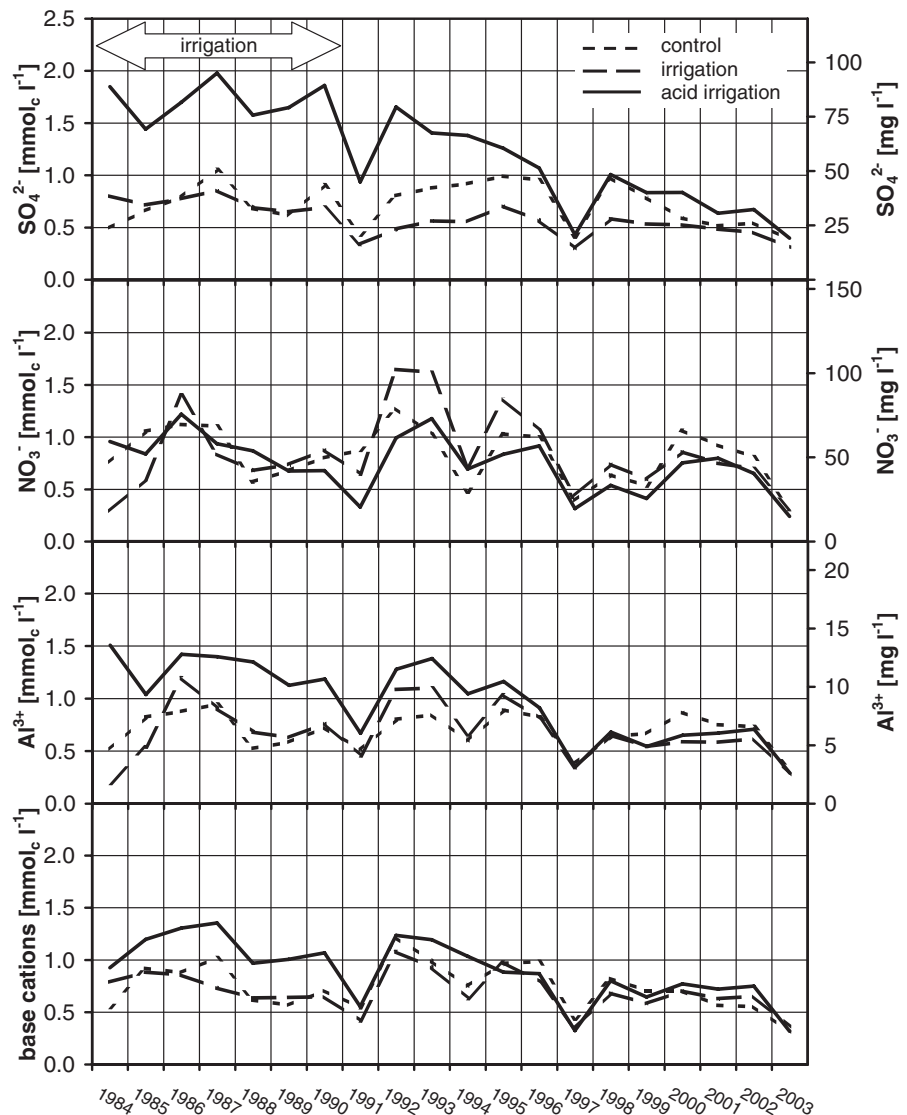
depth during the years of irrigation if compared to the control plot. However, we found lower sulphate concentrations after the end of the experimental irrigation. Together with sulphate, both aluminium and base cations showed enhanced mean annual concentrations during and after the acid irrigation. No effects of the experiment on nitrate concentrations could be detected, probably due to the high inter-annual variance of the values.

In Table 4 the mean annual water and ion fluxes in bulk precipitation, throughfall including irrigation,

and seepage in 40 cm soil depth are presented for the period of experimental irrigation and the period of recovery.

During the experiment (1984–1990), irrigation, both non-acid and acid, generally enhanced the ion fluxes. In comparison to the control plot, both irrigated plots showed higher nitrate fluxes in 40 cm soil depth indicating the positive effect of a well moistened soil on nitrification. In addition, non-acid irrigation increased the sulphate flux in 40 cm soil depth despite an input equal to the control. The

Fig. 4 Flux-weighted annual means of the concentration of sulphate, nitrate, aluminium and base cations (Ca, Mg, K, Na) in the seepage water in 40 cm soil depth on the control, the non-acid irrigated, and the acid-irrigated plot at Höglwald



additional input of protons and sulphate during acid irrigation resulted in fluxes of sulphate in 40 cm even higher than those calculated for the non-acid irrigated plot. However, no remarkably higher proton fluxes could be detected. The difference between the S-output in 40 cm soil depth and the S-input as a measure for the changes in the soil content of total sulphur was $-0.02 \text{ mol}_c \text{ m}^{-2}$ on the control plot, $+0.54 \text{ mol}_c \text{ m}^{-2}$ on the non-acid irrigation plot, and $-0.17 \text{ mol}_c \text{ m}^{-2}$ on the acid irrigation plot. This indicates, that during the experiment the non-acid irrigation lead to a release of sulphur from the soil above 40 cm, whereas during the acid irrigation additional sulphur was stored in the soil. Calculations of the sulphate leaving the humus layer between 1987

and 1990 gave evidence, that none of the additional sulphur had been stored in the organic layer. The elevated fluxes of nitrate and sulphate on the irrigated plots lead to higher fluxes of cations. Quantitatively relevant are the fluxes of aluminium, calcium and magnesium whereas manganese, sodium and potassium play a minor, iron a negligible role. On the non-acid irrigated plot the mean ratio between base cations (Ca+Mg+K) and aluminium (0.93) did hardly differ from the value on the control plot (0.92). Acid irrigation, however, lowered this ratio to 0.79.

In the period of regeneration (1991–2003) element input was assumed to be the same on all plots. No differences in the mean proton fluxes in 40 cm between plots were visible. The non-acid irrigation

Table 4 Mean annual water and element fluxes in bulk precipitation, throughfall, irrigation and seepage in 40 cm soil depth on the control, the non-acid irrigated, and the acid irrigated plot at Höglwald

	Flux [mm a ⁻¹]	H ⁺	Al ³⁺	Fe ³⁺	Mn ²⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
		[mmol _c m ⁻² a ⁻¹]											
Period of experiment: 1984–1990													
bulk precipitation	849	17	5	0.80	1	28	11	9	17	45	15	37	49
throughfall	508	7	4	0.74	10	62	24	40	15	162	28	77	169
throughfall+non-acid irrigation	678	9	5	1.25	10	69	28	42	17	164	30	85	174
throughfall+acid irrigation	678	440	5	1.25	10	70	28	42	18	164	31	83	602
flux 40 cm control	173	8	160	0.22	35	73	68	7	22	4	18	195	166
flux 40 cm non-acid irrigation	321	14	238	0.32	40	109	105	8	29	5	24	259	251
flux 40 cm acid irrigation	321	20	433	0.42	58	161	172	10	38	6	25	298	578
Period of recovery: 1991–2003													
bulk precipitation	989	9	1	2.18	0	20	5	6	9	49	14	37	32
throughfall	585	2	1	1.69	7	40	17	50	13	124	27	75	80
flux 40 cm control	245	16	214	0.66	49	82	104	5	36	2	21	250	218
flux 40 cm non-acid irrigation	245	15	211	0.54	35	87	93	5	28	1	18	276	153
flux 40 cm acid irrigation	245	16	247	0.71	47	96	112	5	31	2	19	211	295

During the period of experiment, non-acid and acid irrigation was carried out May through October

plot showed slightly higher, the acid irrigation plot lower nitrate fluxes than the control. If these effects are genuine, they indicate a long-term stimulation of nitrification by non-acid irrigation and a delayed inhibition of nitrification after acid irrigation. The sulphate fluxes still were highest on the acid irrigation plot and lowest on the non-acid irrigation plot. On all three plots a release of sulphur from the soil was calculated, with 1.79 mol_c m⁻² on the control plot, 0.95 mol_c m⁻² on the non-acid irrigation plot, and 2.80 mol_c m⁻² on the acid irrigation plot. Due to the still elevated sulphur fluxes, cation fluxes on the acid irrigation plot were higher than on the control plot and the non acid-irrigation plot. However, the ratio between base cations (Ca+Mg+K) and aluminium had improved, with 0.86 on the acid irrigation plot compared to 0.90 on the control and 0.87 on the non-acid irrigation plot.

In order to quantify the nutrient losses due to non-acid and acid irrigation we calculated the balance between element input with deposition (excluding canopy leaching) and the element losses due to soil leaching in 40 cm depth and element uptake by the trees (Table 5). In the table a positive balance signifies a net loss from the soil. We have to assume a high uncertainty on the presented values, as the numbers of replicates per plot are not satisfying and the calculated soil water fluxes can not be validated di-

rectly. Therefore we concentrate only on differences between plots of more than 30%. For the 20 years between 1984 and 2003 the mean annual balance was positive for all investigated elements on all three plots. With respect to sulphur the net losses from the soil can be related to the development of the sulphur deposition during the last decades. Between the 1970s and the 1990s, SO₂ emissions declined throughout West Germany. The deposition of sulphate measured in the throughfall at Höglwald since 1984 closely follows this trend (Fig. 1). As a consequence, the water infiltrating into the soil is characterised by decreasing sulphate concentrations, which affects the S-adsorption in the soil. Compared to the control plot, the non-acid irrigation plot showed higher losses of nitrogen of almost 40%, which were accompanied by aluminium, calcium and magnesium. On the acid irrigation plot the mean nitrogen balance was hardly different from the control plot. However, the balance of sulphur was almost 50% higher than that on the control plot. This indicates, that, despite the irrigation with sulphuric acid, the net release of sulphur from the soil is higher than on the control plot. Together with sulphur, we calculated remarkable net losses of calcium and of magnesium, which were 36 and 42% higher than on the control plot. At Höglwald, the supply of exchangeable cations is about 2.5 mol_c m⁻² a⁻¹ (organic layer together with

Table 5 Mean annual element balances on the control, the non-acid irrigated, and the acid irrigated plot at Höglwald (whole observation period 1984–2003)

1984–2003	Al ³⁺	Fe ³⁺	Mn ²⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	N	S
	[mmol _c m ⁻² a ⁻¹]								
Control									
deposition	2	1	1	29	8	9	14	213	111
output 40 cm	195	1	44	79	92	6	31	233	200
element uptake	1	1	9	53	11	8	0	74	n.d.
balance	194	1	52	103	95	5	17	94	89
Non-acid irrigation									
deposition	2	1	1	32	9	10	15	216	113
output 40 cm	221	0	37	94	97	6	29	272	187
element uptake	1	1	9	53	11	8	0	74	n.d.
balance	220	0	45	115	99	4	14	130	75
Acid irrigation									
deposition	2	1	1	32	9	10	15	215	262
output 40 cm	312	1	51	119	133	6	33	245	394
element uptake	1	1	9	53	11	8	0	74	n.d.
balance	311	1	59	140	135	4	18	103	131

The calculation of deposition and element uptake is explained in the methodology section

the first 40 cm of the mineral soil). On all three plots it changed only insignificantly over time (slope of the trend line: 0.005 mmol_c m⁻² a⁻¹). Despite the higher losses of base cations on the acid irrigation plot, no additional decrease in the supply of exchangeable base cations could be detected in comparison to the control plot (Fig. 3).

4 Discussion

Our investigations suffer from a number of shortcomings: We have no pre-treatment measurements, no treatment replications were possible due to limited space and financing, and the number of replicates used for the different measurements on the specific plots is considerably small and changing in time. As a consequence we did no statistical evaluation of our results. Nevertheless, we think that the large number of investigations and the long observation period allows a well-founded interpretation of the results.

If we look at the impact of the experimental irrigation with sulphuric acid at Höglwald on the element cycling in the soil, the combined impact of high proton input and deposition of sulphate have to be considered.

Despite the considerable input of acidity, effects on soil pH and proton fluxes in 40 cm soil depth are low. Most of the protons are buffered either by cation exchange in the organic layer or by dissolution of aluminium-hydroxides in the mineral soil (Kreutzer et al. 1989). As a further mechanism, Kreutzer et al. (1991) proposes the reduction of the ammonium uptake by tree roots in the organic soil. The observed reduction of the cation exchange capacity in the organic layer may be due to a change of the pK_s values of organic functional groups and due to the protonation of weak organic acids, e.g. carboxyl groups of the organic material (Kreutzer et al. 1989, 1991; James and Riha 1986). As a consequence of the still high buffering capacity at Höglwald, no persistent changes in the soil pH occurred.

Following our flux calculations, the additional deposition of sulphate led to a small increase in the adsorbed sulphur in the mineral soil during the years of the acid irrigation experiment. Of the 530 kg ha⁻¹ of additional sulphur input during the seven years of acid irrigation only 27 kg ha⁻¹ stayed in the soil above 40 cm. No net sulphur adsorption was calculated on the control plot and the non-acid irrigation even generated a net sulphur release of 86 kg ha⁻¹. These results suggest that the major factor

controlling sulphate adsorption during the irrigation experiments at Höglwald is the sulphate concentration in the seepage water. A possible pH-effect is of minor importance as (1) the changes of the pH in soil and soil water are small, and (2) the slope of the relationship between pH and sulphate adsorption is small at pH-values near 4.2 (Nodvin et al. 1986). Results from an investigation of the sulphur pools on the control plot and the acid irrigation plot in 1986 suggest a complete adsorption of the amount of sulphur additionally deposited between 1984 and 1986 in the soil above 50 cm (Fischer and Pecht 1991). This is in conflict with the observation of elevated sulphate concentrations and fluxes in the seepage water in 40 cm depth. As no investigations of the sulphur supply on the two plots prior to the treatment were carried out, the natural variation may explain this contradiction. Data from a lysimeter study using soil from the Höglwald site and simulating three different scenarios of sulphur deposition (23, 42, and 87 kg SO₄-S ha⁻¹ a⁻¹) gives little evidence that an enhanced deposition of sulphur increases the amount of total soil sulphur at Höglwald. However, the experiment, using labelled sulphate, indicates that large amounts of the deposited sulphur are not transferred directly towards deeper soil horizons together with the seepage water, but exchange with the sulphur already adsorbed in the soil, predominantly with inorganic sulphate adsorbed at Fe and Al oxides and hydroxides. It has also to be taken into account, that the deposited amounts of sulphur are small compared to the total mass of sulphur in the soil (Mayer et al. 1995, 2001).

After the end of the experimental irrigation, the calculated sulphate fluxes in 40 cm soil depth exceeded the input with throughfall on all three plots. During the 13 years of observation, 156, 82, and 241 kg S ha⁻¹ were released from the soil on the control, non-acid irrigation and acid irrigation plot, respectively. Again we attribute this release of sulphur from the soil to decreasing sulphate concentration in throughfall and seepage water. Similar observations are known from 'clean-rain' experiments (Beier et al. 1998; Boxman et al. 1995) and a couple of long time experiments in North America and Europe (Cooper 2005; Driscoll et al. 2003; Hrkál 2004; Likens et al. 2002; Novak et al. 2000; Park et al. 2003; Prechtel et al. 2001). Surprisingly, the overall release of sulphur from the soil between 1984 and 2003 was

highest on the acid irrigation plot suggesting that the temporal acid irrigation enhanced sulphur desorption. We can only speculate about the reasons behind. Possibly not only the actual sulphate concentration in the water percolating the soil but also the magnitude of its decline with time is important for sulphur desorption processes. Alternately or in addition, the protonation of organic material during the acid irrigation as discussed above and the competition of sulphate and dissolved organic carbon (DOC) for similar adsorption sites in the soil (Evans 1986; Göttlein and Matzner 1997; Johnson and Todd 1983) may be responsible for an enhanced sulphur desorption. Low pH values inhibit the mobilisation of organic carbon as DOC (Lofts et al. 2001). An enrichment of potentially mobilisable organic components in the organic layer during the acid irrigation seems possible. After the end of the acid irrigation, deprotonation may take place, surplus DOC may enter the mineral soil and there exchange against sulphate.

Together with sulphate both aluminium and base cations are leaving the main rooting zone. This indicates the involvement of two processes in the buffering of the high acidity input: (1) Especially in the organic layer, where cation exchange capacity and base saturation is high, protons are exchanged against base cations (mostly calcium and magnesium) adsorbed at the exchange sites of the soil. (2) In the already acidified upper mineral soil, acidity is buffered by aluminium hydroxides and other aluminium compounds. Aluminium concentrations measured in 40 cm soil depth are well over the drinking water standard of the European Union (0.2 mg l⁻¹). However, due to high amounts of exchangeable calcium and magnesium in the soil below 40 cm at Höglwald, most of the aluminium is exchanged there and aluminium concentrations in deeper soil layers never surpass the critical value (Kreutzer et al. 1998). High aluminium concentrations and, especially, low molar ratios between the concentrations of base cations and aluminium are supposed to inhibit tree growth (Sverdrup and Warfvinge 1993). Spranger et al. (2004) suggests a critical molar ratio between Ca+Mg+K and aluminium of 1.0 for coniferous forests. However, several authors challenge this approach (De Wit et al. 2001; Göransson and Eldhuset 2001; Högborg and Jensén 1994; Løkke et al. 1996). At the Höglwald control plot the respective ratio in the seepage water in

40 cm was clearly below 1.0. Acid irrigation further reduced the value below 0.8. Nevertheless, no inhibitional effects of the acid irrigation on tree growth, nutrition and crown transparency could be detected (Huber et al. 2004a). Investigations of root growth (Hahn and Marschner 1998a; Nowotny et al. 1998) and cation concentrations in short roots (Hahn and Marschner 1998b) carried out directly after the end of our acid irrigation experiment gave little evidence of lasting reactions to the acid irrigation. As summarised by Hahn and Marschner (1998a), there are several explanation for the apparent stability of the Höglwald spruce stand against high acid depositions. Though the upper mineral soil is strongly acidified, base saturation reaches more than 50% in 70 cm soil depth, which is still in reach of the root system. Consequently, not the whole root system suffers from high aluminium and low base cation concentrations. In addition, soil solution chemistry in the rhizosphere can be completely different from the composition measured in suction cup lysimeters. A possible complexation with organic compounds or sulphate, which is present at high concentrations, will render aluminium ions non-phytotoxic.

The enhanced losses of calcium and magnesium from the soil above 40 cm after experimental acidification did not result in a prolonged decrease of the cation exchange capacity or the base saturation in comparison to the control plot. The observed decline in cation exchange capacity in the organic layer during the years of acid irrigation 1984 through 1990 was followed by a complete recovery until 2004. Thus, mechanisms other than the irreversible depletion of the exchangeable pool of base cations have to be involved in the release of calcium and magnesium. Possible sources for base cations are: (1) A temporarily enhanced decomposition of organic material probably supplies base cations without a long term change in cation exchange capacity and base saturation. This would imply enhanced mineralisation rates in the organic horizons. However, no changes in the microbiological activity due to acid irrigation have been reported at Höglwald (Anderson 1998). (2) The elevated soil water content and the excessive proton input during acid irrigation will intensify weathering reactions (Sverdrup and Warfvinge 1995) and thus release additional base cations. (3) The temporal acidification of the upper soil horizons and the

unfavourable ratio between base cations and aluminium may reduce the base cation nutrient uptake in the upper soil horizons. As forest growth and nutrition was not affected by acid irrigation (Huber et al. 2004a) this would have to be compensated by higher uptake rates in the lower mineral soil or by decreased base cation contents in biomass compartments which so far have not been analysed on this plot, e.g. bark and wood.

5 Conclusions

The acid irrigation experiment at the ‘Höglwald,’ a well nourished, mature Norway spruce stand in Bavaria, Southern Germany, corroborates the acidification hypothesis formulated by Ulrich (1983a) in so far, that an additional acidity input leads in fact to a reduction of the ratio between base cations and aluminium and to an enhanced base cation and aluminium leaching in soil horizons characterised by a low base saturation. However, neither tree growth and nutrition nor the supply of exchangeable base cations in the main rooting zone were affected significantly. The high proton buffering capacity of the site prevented a drop in soil pH unfavourable in magnitude to tree health. We conclude that at this site protection mechanisms against aluminium toxicity exist and that additional base cation runoff can still be compensated without further reduction of the cation exchange capacity or the base saturation in the upper mineral soil.

Acknowledgements Research at the “Höglwald” was funded by the Federal Department for Education and Research, Berlin, and the Bavarian State Ministry for Agriculture and Forestry, Munich.

References

- Anderson, T.-H. (1998). The influence of acid irrigation and liming on the soil microbial biomass in a Norway spruce (*Picea abies* [L.] K.) stand. *Plant and Soil*, 199, 117–122.
- Beier, C., Blanck, K., Bredemeier, M., Lamersdorf, N., Rasmussen, L., & Xu, Y.-J. (1998). Fiedl-scale ‘clean rain’ treatments to two Norway spruce stands within the EXMAN project – effects on soil solution chemistry and tree growth. *Forest Ecology and Management*, 101, 111–123.
- Boxman, A. W., van Dam, D., van Dijk, H. F. G., Hogervorst, R. F., & Koopmans, C. J. (1995). Ecosystem responses to reduced nitrogen and sulphur inputs into two coniferous

- forest stands in the Netherlands. *Forest Ecology and Management*, 71, 7–29.
- Cooper, D. M. (2005). Evidence of sulphur and nitrogen deposition signals at the United Kingdom Acid Waters Monitoring Network sites. *Environmental Pollution*, 137, 41–54.
- De Wit, H. A., Mulder, J., Nygaard, P. H., Aamlid, D., Huse, M., Kortnes, E., et al. (2001). Aluminium: The need for a re-evaluation of its toxicity and solubility in mature forest stands. *Water, Air, and Soil Pollution: Focus*, 1, 103–118.
- Driscoll, C. T., Driscoll, K. M., Mitchell, M. J., & Raynal, D. J. (2003). Effects of acid deposition on forest and aquatic ecosystems in New York State. *Environmental Pollution*, 123, 327–336.
- Evans, A. (1986). Effects of dissolved organic carbon and sulfate on aluminium mobilization in forest soil columns. *Soil Science Society of America Journal*, 50, 1576–1578.
- Fischer, M., & Pecht, K. (1991). Soil-sulfur status of different 'Höglwald'-plots. Influence of tree species and simulated acid rain. In K. Kreutzer & A. Göttelein (Eds.), *Ökosystemforschung Höglwald* (pp. 228–236). Hamburg, Berlin, Germany: Paul Parey Verlag.
- Göransson, A., & Eldhuset, T. D. (2001). Is the Ca+K+Mg/Al ratio in the soil solution a predictive tool for estimating forest damage? *Water, Air, and Soil Pollution: Focus*, 1, 57–74.
- Göttelein, A., & Matzner, E. (1997). Microscale heterogeneity of acidity related stress-parameters in the soil solution of a forested cambic podsol. *Plant and Soil*, 192, 95–105.
- Hahn, G., & Marschner, H. (1998a). Effect of acid irrigation and liming on root growth of Norway spruce. *Plant and Soil*, 199, 11–22.
- Hahn, G., & Marschner, H. (1998b). Cation concentrations of short roots of Norway spruce as affected by acid irrigation and liming. *Plant and Soil*, 199, 23–27.
- Högberg, P., & Jensen, P. (1994). Aluminium and uptake of base cations by tree roots: A critique of the model proposed by Sverdrup et al. *Water, Air, and Soil Pollution*, 75, 121–125.
- Hrkál, Z. (2004). Changes in acid atmospheric deposition in Krušné Mts. And Šumava (Czech Republic) and their impact on groundwater quality. *Water, Air, and Soil Pollution*, 157, 163–178.
- Huber, C., Röhle, H., Rothe, A., & Kreutzer, K. (2004a). Response of nitrogen fertilisation, irrigation, acid irrigation and forest liming on the nutritional status, litter fluxes, growth and health status of a nitrogen saturated Norway spruce stand in Southern Bavaria (Höglwald). *Forest Ecology and Management*, 200, 3–21.
- Huber, C., Weis, W., Baumgarten, M., & Göttelein, A. (2004b). Spatial and temporal variation of seepage water chemistry after felling and small scale clear-cutting in a N-saturated Norway spruce stand. *Plant and Soil*, 267, 23–40.
- James, B. R., & Riha, S. (1986). pH buffering in forest soil organic horizons: Relevance to acid precipitation. *Journal of Environmental Quality*, 15, 229.
- Johnson, D. W., & Todd, D. E. (1983). Relationship among iron, aluminium, carbon and sulfate in a variety of forest soils. *Soil Science Society of America Journal*, 47, 792–800.
- Kreutzer, K., Beier, C., Bredemeier, M., Blanck, K., Cummins, T., Farrell, E. P., et al. (1998). Atmospheric deposition and soil acidification in five coniferous forest ecosystems: A comparison of the control plots of the EXMAN sites. *Forest Ecology and Management*, 101(1–3), 125–142.
- Kreutzer, K., Göttelein, A., & Pröbstle, P. (1991). Effects of acid irrigation on soil chemistry in a Norway spruce stand (*Picea abies* [L.] Karst.). In K. Kreutzer & A. Göttelein (Eds.), *Ökosystemforschung Höglwald* (pp. 174–186). Hamburg, Berlin, Germany: Paul Parey Verlag.
- Kreutzer, K., Reiter, H., Schierl, R., & Göttelein, A. (1989). Effects of acid irrigation and liming in a Norway spruce stand (*Picea abies* [L.] Karst.). *Water, Air, and Soil Pollution*, 48, 111–125.
- Kreutzer, K., & Weiss, T. (1998). The Höglwald field experiments – aims, concepts and basic data. *Plant and Soil*, 199, 1–10.
- Likens, G. E., Driscoll, C. T., Buso, D. C., Mitchell, M. J., Lovett, G. M., Bailley, S. W., et al. (2002). The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry*, 60, 235–316.
- Lofts, S., Simon, B. M., Tipping, E., & Woof, C. (2001). Modelling the solid-solution partitioning of organic matter in European forest soils. *European Journal of Soil Science*, 52, 215–226.
- Lökke, H., Bak, J., Falkengren-Grerup, U., Finley, R. D., Ilvesniemi, H., Nygaard, P. H., et al. (1996). Critical loads of acid deposition for forest soils: Is the current approach adequate? *Ambio*, 25, 510–516.
- Mayer, B., Fritz, P., Prietzel, J., & Krouse, H. R. (1995). The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. *Applied Geochemistry*, 10, 161–173.
- Mayer, B., Prietzel, J., & Krouse, H. R. (2001). The influence of sulfur deposition rates on sulfate retention patterns and mechanisms in aerated forest soils. *Applied Geochemistry*, 16, 1003–1019.
- Nair, V. D., & Prenzel, J. (1978). Calculations of equilibrium concentrations of mono- and polynuclear hydroxoaluminium species at different pH and total aluminium concentrations. *Zeitschrift für Pflanzenernährung und Bodenkunde*, 141, 741–751.
- Nodvin, S. C., Driscoll, C. T., & Likens, G. E. (1986). The effect of pH on sulfate adsorption by a forest soil. *Soil Science*, 142(2), 69–75.
- Novak, M., Kirchner, J. W., Groscheová, H., Havel, M., Černý, J., Krejčí, R., et al. (2000). Sulfur isotope dynamics in two Central European watersheds affected by high atmospheric deposition of SO_x. *Geochimica et Cosmochimica Acta*, 64(3), 367–383.
- Nowotny, I., Dähne, J., Klingelhöfer, D., & Rothe, G. M. (1998). Effect of artificial acidification and liming on growth and nutrient status of mycorrhizal roots of Norway spruce (*Picea abies* [L.] Karst.). *Plant and Soil*, 199, 29–40.
- Park, J. I.-H., Mitchell, M. J., McHale, P. J., Christopher, S. F., & Meyers, T. P. (2003). Impacts of changing climate and atmospheric deposition on N and S drainage losses from a forested watershed of the Adirondack Mountains, New York State. *Global Change Biology*, 9, 1602–1619.
- Prechtel, A., Alewell, C., Armbruster, M., Bittersohl, J., Cullen, J. M., Evans, C. D., et al. (2001). Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrology and Earth System Science*, 5(3), 311–325.

- Reuss, J. O., & Johnson, D. W. (1986). Acid deposition and the acidification of soils and waters. In *Ecological Studies* Vol. 59, (119 pp). Berlin Heidelberg New York: Springer.
- Spranger, T., Lorenz, U., & Gregor, H.-D. (Eds.) (2004). *Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends* (266 pp.) Berlin, Germany: Federal Environmental Agency.
- Sverdrup, H., & Warfvinge, P. (1993). The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. *Reports in Ecology and Environmental Engineering*, Vol. 2, (177 pp). Lund, Sweden.
- Sverdrup, H., & Warfvinge, P. (1995). Estimating field weathering rates using laboratory kinetics. In A. F. White & S. L. Brantley (Eds.), *Chemical weathering rates of silicate minerals, Reviews in mineralogy* Vol. 31 (pp. 485–541). Washington D. C.: Mineralogical Society of America.
- Ulrich, B. (1983a). Soil acidity and its relations to acid deposition. In B. Ulrich & J. Pankrath (Eds.), *Effects of accumulation of air pollutants in forest ecosystems* (pp. 127–143). Dordrecht: Reidel.
- Ulrich, B. (1983b). Interaction of forest canopies with atmospheric constituents: Alkali and earth alkali cations and chloride. In B. Ulrich & J. Pankrath (Eds.), *Effects of accumulation of air pollutants in forest ecosystems*. Dordrecht: Reidel.
- Umweltbundesamt (Ed.) (1997). *Daten zur Umwelt – Der Zustand der Umwelt in Deutschland* (pp. 135–136). Berlin: Erich Schmitt Verlag.
- van Breemen, N., Mulder, J., & Driscoll, C. T. (1983). Acidification and alkalization of soils. *Plant and Soil*, 75, 283–308.

Nitrogen Budget of a Spruce Forest Ecosystem After Six-year Addition of Ammonium Sulphate in Southwest Sweden

Johan Bergholm · Hooshang Majdi ·
Tryggve Persson

Received: 17 June 2005 / Accepted: 12 August 2006 / Published online: 10 January 2007
© Springer Science + Business Media B.V. 2007

Abstract A nitrogen (N) budget was constructed for a period of 6 years (1988–1993) in a Norway spruce stand with current deposition of 19 kg N and 22 kg S $\text{ha}^{-1} \text{year}^{-1}$. The stand was fertilized annually by addition of 100 kg N and 114 kg S ha^{-1} (NS). Above and below ground biomass, litterfall, fine-root litter production, soil solution and net mineralization were measured to estimate pools, fluxes and accumulation of nitrogen. The average needle litterfall in control (C) and NS plots in 1993 was 2.2 and 2.5 $\text{ton ha}^{-1} \text{year}^{-1}$, respectively. The fine root litter production prior to treatment (1987) was 4.4 $\text{ton ha}^{-1} \text{year}^{-1}$ and after treatment (1993) it was 4.5 and 3.9 $\text{ton ha}^{-1} \text{year}^{-1}$ in C and NS plots, respectively. Net N mineralization in the soil profile down to 50 cm was estimated to be 86 and 115 $\text{kg ha}^{-1} \text{year}^{-1}$ in C and NS plots, respectively in 1992. During the treatment period the uptake of N in the needle biomass in C and NS plots was 29 and 77 $\text{kg ha}^{-1} \text{year}^{-1}$, respectively. No N was accumulated in needles of C plot where the NS plots accumulated 34 $\text{kg ha}^{-1} \text{year}^{-1}$. Of the annually added inorganic N to NS plots 47% was accumulated in the above and below ground biomass

and 37% in the soil. N fluxes via fine-root litter production in the C plots were much higher (54 $\text{kg ha}^{-1} \text{year}^{-1}$) than that via litterfall (29 $\text{kg ha}^{-1} \text{year}^{-1}$). The corresponding values in the NS plots were 65 and 43 $\text{kg ha}^{-1} \text{year}^{-1}$, respectively. Most of the net N mineralization occurred in the FH layer and upper mineral soil. It is concluded that fine root litter and litterfall play an important role in the cycling of N. Despite a high N uptake the losses of N in litterfall and fine root litter resulted in an incorporation of N in soil organic matter.

Keywords above-ground biomass · ammonium sulphate · budget · fine roots · N flux · N mineralization · pools · spruce

1 Introduction

Nitrogen is generally a limiting nutrient for plant growth but increasing nitrogen deposition may cause nitrogen saturation and ecosystem disturbances (Aber, Nadekhoffer, Steudler, & Melillo, 1989; Ågren, Bosatta, & Magill, 2001) resulting in nitrate leaching and depletion of base cations. Acid deposition in forest soils in Southern Sweden has resulted in lower pH and base saturation (Falkengren-Grerup, 1987; Hallbäcken & Tamm, 1986) and increasing aluminium concentrations in the soil solution. The deposition of base cations has decreased over several decades

J. Bergholm · H. Majdi (✉) · T. Persson
Department of Ecology and Environmental Research,
Swedish University of Agricultural Sciences,
P.O. Box 7072, SE-750 07 Uppsala, Sweden
e-mail: Hooshang.Majdi@eom.slu.se

(Hedin et al., 1994). The increased input of nitrogen and the decreased surplus of base cations may result in nutrient imbalances in the trees.

Ammonium has a fertilising effect on forest stands when nitrogen availability is limited, while a surplus of N represents a potential stress factor which may lead to unbalanced nutrient supply (Aber et al., 1989; Nihlgård, 1985). N saturation in this context is defined as the availability of ammonium and nitrate in excess of plant and microbial utilisation (Aber et al., 1989). The effects of nitrogen on tree nutrition, fine roots, soil and soil solution has been studied in different forest experiments (Wright & Rasmussen, 1998) and in forest ecosystems (Magill et al., 1997; Magill, Downs, Nadelhoffer, Hallet, & Aber, 1996). Addition of N combined with, potassium (K) and phosphorus (P) often increased tree production (Tamm, 1991). In many long-term N experiments (cf. Magill et al., 1996; Magill, Aber, Berntson, Mc Dowell, Nadelhoffer, Melillo, et al., 2000; Magill et al., 2004) fine root turnover has been indirectly calculated based on fine root biomass. In our study we have directly measured root turnover using minirhizotron technique and soil cores (Majdi, 1996). Furthermore, data on long term effects of ammonium sulphate on N pools and fluxes are limited.

This study was a part of a multidisciplinary ecosystem research program (Skogaby project). The objectives of this program (cf. Bergholm et al., 1995) were: (1) to study the impact of air pollution on tree vitality and forest production by selectively applying nutrients to the soil in a Norway spruce stand; (2) to determine which climatic and nutritional conditions result in positive or negative effects of air pollutants on forest growth and vitality; and (3) to determine how to improve tree vitality. The treatments in the present study were designed to reduce availability of other nutrients by nitrogen and sulphur addition (ammonium sulphate). The Skogaby forest experiment included other treatments as nitrogen-free fertilisation, irrigation, irrigation + fertilisation (Bergholm et al., 1995; Majdi, Damm, & Nylund, 2001; Nilsson & Wiklund, 1994).

The aim of the present work was to determine N accumulation and fluxes in above- and below ground tree parts, net N mineralization and soil solution in a Norway spruce stand subjected to (a) ambient deposition and (b) repeated ammonium sulphate addition over a 6-year period.

2 Materials and Methods

2.1 Site Description

The Skogaby site is a second-rotation Norway spruce stand planted in 1966 in southwest Sweden (latitude 56° 33' N, longitude 13° 13' E, altitude 95–115 m above sea level. Open field deposition of S and N at the end of the 1980s was 12 and 13 kg ha⁻¹, respectively (Bergholm et al., 1995), and the annual mean throughfall deposition of N for the period 1989 to 1993 was 18.9 kg ha⁻¹.

The soil type is a Haplic podzol (FAO-Unesco, 1990) on a loamy sandy till with 4% clay. The pH (H₂O) prior to treatments was 3.9 in the Oa horizon and 4.1 in the upper 10 cm of the mineral soil and 4.5 at 50 cm depth. The effective base saturation was 30% in the Oa and varied from 8 to 12% from 10 to 50 cm depth in the mineral soil. Further physical and chemical characteristics of the soil are described by Bergholm et al. (1995).

The site was planted in 1966 with two Polish provenances of Norway spruce (*Picea abies* (L.) Karst.). At the start of the experiment in 1988, the age of the spruce trees was 25 years.

The experiment had a randomised block design with four replicates. The plot size of 45×45 m² with a smaller area (12.5×12.5 m²) was used for measurement of tree growth, throughfall and litterfall. All destructive sampling within a plot (except soil sampling) was performed outside the small area. The treatments used in this study were control (C) and ammonium sulphate application (NS). Ammonium sulphate in solid form was added manually in three portions in (May, June and July) every year for 6 years, starting in 1988. The annual application rate was 100 kg N and 114 kg S ha⁻¹ (Bergholm et al., 1995) and the total amount added by 1993 was 600 kg N and 684 kg S ha⁻¹.

2.2 Deposition

Bulk and throughfall deposition was sampled by four collectors (bulk deposition in the open field) and six collectors per plot (throughfall) in C during 1989–1993 and in NS during 1989–1990 and 1993. The collectors consisted of a polyethene funnel 20 cm in diameter and a container in a dark box placed on the forest floor. Deposition was collected every fortnight

during June–September and every month during the rest of the year.

Mean annual deposition of inorganic N was about 17 and 22 kg ha⁻¹ in the C and NS plots, respectively, during 1989–1993. Corresponding values for dissolved organic N were 2.2 and 0.5 kg ha⁻¹ year⁻¹, respectively. The throughfall of ammonium increased gradually in the NS plots during the study period (not shown). The deposition of N taken up by the canopy was not measured.

2.3 Biomass

Above-ground biomass of stem, bark, twigs, branches and needle was measured by destructive sampling of whole trees (cf. Nilsson & Wiklund, 1992, 1994).

Coarse root (>2 mm in diameter) biomass (kg tree⁻¹) was estimated by using logarithmic equations (Marklund, 1987, 1988) for roots >5 cm ($\ln y = 13.37d/(d+8) - 6.39$) and <5 cm ($\ln y = 7.63d/(d+12) - 2.57$) with stem diameter (d) at breast height as independent variable.

Fine roots (<2 mm) were sampled, using soil cores in humus and mineral soil layers. During 1987 (before start of the experiment) and 1989, 1990 and 1992 ten core samples were taken in each plot. Cylindrical cores 7.2 cm in diameter were taken from the humus layer at depth of about 4 cm. Cores of 4.5 cm in diameter were sampled from the stony underlying mineral soil at depths of 0–10, 10–20 and 20–30 cm. The zero depth refers to the boundary between the humus layer and mineral soil. The subsamples were carefully transferred into plastic bags. The samples were stored at -18°C. Before processing and sorting the samples were placed at +4°C for about 4 h. For more details see Majdi and Persson (1995).

2.4 Litterfall and Fine-root Litter Production

Litterfall data was measured during 1988–1993 using nine circular litter traps (0.25 m² in size) within the experimental unit in each plot and collected 11 times year⁻¹. The litterfall was separated into needles and twigs and branches (Table 1).

Table 1 Means (±S.E.) of above- and below-ground biomass (ton DW ha⁻¹), nitrogen pool (kg ha⁻¹), litterfall and fine-root litter production (ton DW ha⁻¹year⁻¹), during 1987–1993 in C and NS plots

	1987	1993	
	Prior to treatment	Treatment	
		C	NS
Above-ground biomass (ton ha ⁻¹)			
Stem, bark, branches and twigs	72±8.4	108±10.8	121±15.2
Needle	14.5±0.8	14±1.1	17±1.4
Below-ground biomass (ton ha ⁻¹)			
Coarse root (>2 mm) ^a	19±2.2	28±2.8	30±3.8
Fine root (<2 mm)	4.9±0.3	5.1±0.3*	4.9±0.2*
Nitrogen pools (kg ha ⁻¹)			
Stem, bark, branches and twigs	180±21	210±21	302±38
Needle	172±9.5	174±14	376±31
Coarse root (>2 mm)	45±5.2	55±5.5	76±9.7
Fine root (<2 mm)	71±4.3	48±2.8*	57±2.1*
Total	468±32	487±33	811±61
Litter production (ton ha ⁻¹ year ⁻¹)			
Litterfall			
Needles		2.2±1.0	2.5±1.2
Twigs and branches		0.2±0.1	0.2±0.1
Fine-root litter production	4.4±0.3	4.5±0.2*	3.9±0.1*

Litterfall data from Nilsson and Wiklund (1992, 1994)

*Average for 1989–1992

^aEstimated by regressions (see Section 2)

The fine root litter was estimated by multiplying the annual average of fine root biomass from 1987 to 1992, by the estimated turnover (year^{-1}) of fine roots. Fine root turnover was estimated as the inverse of median root longevity obtained by minirhizotron technique during 1991–1993. The turnover was estimated at 0.9 and 0.8 year^{-1} , in C and NS plots, respectively (Majdi & Kangas, 1997).

2.5 Soil Sampling

Soil samples were taken on two occasions, in 1987 (prior to the treatment) and 1993. Volume -based composite samples of forest floor (FF) were taken ($n=40$) using a steel cylinder (5.6 cm diameter). Mineral soil composite samples ($n=20$) were taken to 50 cm depth using a soil core sampler (2.8 cm in diameter) and were divided into five 10-cm layers. In 1993 the sampling of FF was split up into litter (L) and humus (FH) layers.

The composite samples per plot were sieved fresh, FF, L and FH through a 4 mm mesh and mineral soil through a 2 mm mesh. The soil samples were dried at 40°C. The surface-related amount of fine mineral soil was calculated using bulk density of the different layers and the stoniness of the upper 30 cm of each plot estimated by the rod method (Viro, 1952) in combination with the calculated stone volume in 12 pits to a depth of 1 m.

2.6 Soil Solution

Six lysimeters per plot were installed at 50 cm depth starting in August 1988. Soil solution was measured by suction lysimeters equipped with ceramic caps of P80 material (CeramTec, Germany). The lysimeters were operated at a transient vacuum during one week using an initial tension of about -70 kPa. The six samples per plot were pooled by equal volumes and were stored in a freezer (-18°C) prior to chemical analyses.

2.7 Net N Mineralization

At each plot, four soil samples were taken to a depth of 50 cm in the mineral soil in April 1992. L and FH layers were generally sampled by taking the materials within a ring covering 250 cm^2 . Mineral soil layers were sampled by a soil corer of 15.9 cm^2 cutting edges and were divided into 0–10, 10–20, 20–30 and

30–50 cm depth. Samples of litter and soil from the same plot and soil layer were pooled. The fresh L samples were sorted free from green parts and branches. Samples from all other soil layers were sieved. The FH layer was sieved through a 5-mm mesh and the mineral soil through a 2-mm mesh, whereby roots, stones and buried branches were removed.

Litter, humus and mineral soil subsamples (corresponding to 6, 16 and 100 g dry wt, respectively) were placed in plastic jars (50 cm^2 surface area, 466 cm^3 volume). The jars had a lid with a 5-mm diameter aperture for gas exchange. These soil microcosms were incubated in the lab at constant temperature (15°C) and moisture (60% WHC, water-holding capacity). Distilled water was added once a month to keep the water content in the samples constantly high. A whole incubation period lasted for about 140 days. A destructive sampling was also made about 50 days after the start of the incubation, and this shorter period was used for calculation of the accumulation rates of inorganic N. Because no leaching could occur in the jars, inorganic N accumulated in the samples, and the accumulation rate was considered as net N mineralization rate.

2.8 Chemical Analysis

Dissolved organic N (DON), NH_4^+ and NO_3^- , were determined by flow injection analysis (FIA STAR). Total N in biomass and soil samples was analyzed using an elemental C/N analyser (Carlo Erba, NA 1500).

2.9 Budget Calculations

2.9.1 Nitrogen Pools

The amount of N in above-ground biomass in 1987 and 1993 was estimated using the amount of biomass in the individual plots multiplied by the N concentrations of stems, twigs, branches and needles (Nilsson & Wiklund, 1992).

The amount of N in the coarse root biomass ($>2\text{ mm}$) was estimated by the weighted mean concentration of N in stem, bark and living branches (biomass-weighted mean) multiplied by the estimated coarse root biomass.

The amount of N in living fine roots was estimated by multiplying the mean N concentration with the

average fine-root biomass in 1987, 1989, 1990 and 1992.

The amount of N in soil was estimated as the N concentration per soil layer times the amount of soil of the layer.

2.9.2 N Accumulation

The annual accumulation of N in the different above-ground biomass compartments and coarse roots were calculated as the difference between the amount of N in 1987 and 1993.

The amount of N in fine roots was calculated as the difference between 1987 and an average amount of 1989, 1990 and 1992.

The N accumulation in soil in NS plots was calculated as the difference between NS and C for the year 1993.

2.10 N Fluxes

Deposition of N was calculated as the amount of precipitation multiplied by the weighted mean concentration of DON, $NH_4^+ - N$ and $NO_3^- - N$.

N in the litterfall of needles, twigs and branches were calculated by multiplying N concentrations with the pool size of each compartment. N in fine-root litter production was estimated as the average of N concentration in fine roots multiplied by fine root turnover ($\text{kg ha}^{-1} \text{ year}^{-1}$).

Net N mineralization was extrapolated to the field by multiplying the rates obtained in the laboratory by (1) the amount of soil layer and (2) a temperature/moisture-dependent factor calculated with input data from (a) soil temperature and soil moisture measurements in the field and (b) a response function for temperature and moisture (given as eq. 2 in Persson et al., 2000).

Nitrogen leaching from the 50 cm depth was calculated using the concentration of DON, $NH_4^+ - N$ and $NO_3^- - N$ linearly interpolated on a daily basis between sampling occasions, multiplied by the estimated daily flow of soil water at the same depth. The flow of soil water was estimated from simulations by the SOIL-model (Jansson, 1998). The model consists of two differential equations describing vertical flow of water and heat with the daily sum of precipitation and daily mean air temperature, air humidity, wind speed and global radiation as driving variables.

The remaining fluxes were calculated from net changes in pool sizes and known fluxes.

2.10.1 Statistical Analyses

The data obtained were statistically analysed in a randomized block design. Means of pools and fluxes, above and below ground biomass, litterfall and root production, net N mineralization, for each treatment were calculated by averaging means of plots ($n=4$). Statistical analyses were carried out using the General Linear Model as implemented in SAS software (GLM; SAS, 2002). Pairwise comparisons between all treatment means ($n=4$) were made by Tukey's HSD tests ($p<0.05$).

3 Results and Discussion

3.1 Biomass and Litter Production

Above-ground biomass and needle biomass (ton ha^{-1}), (1992 data taken from Nilsson and Wiklund, and delivered by L. O. Nilsson for 1993), coarse- and fine-root biomass (ton ha^{-1}) in 1987 (before treatment) and 6 years after treatment are shown in (Table 1). The above-ground biomass increased during this period by 41 and 59% in C and NS, respectively and the difference in biomass increment between treatments was significant ($p<0.05$). However, the increase after 6 years treatment was 45% higher in NS than C plots but not significant.

The fine-root biomass was almost similar in 1993 as in 1987 in both C and NS. On the other hand NS treatment resulted in a significant ($p<0.05$) increase in the N turnover via fine roots (Majdi & Kangas, 1997).

Average needle litterfall was estimated to be 2.2 and 2.5 $\text{ton ha}^{-1} \text{ year}^{-1}$ (1989–1993) in the C and NS treatments, respectively (Table 1), while the litterfall of other compartments, e.g., twigs and branches was 0.2 $\text{ton ha}^{-1} \text{ year}^{-1}$. The fine-root litter production prior to treatment (1987) was estimated to be 4.4 $\text{ton ha}^{-1} \text{ year}^{-1}$ and in 1992 it was 4.5 and 3.9 $\text{ton ha}^{-1} \text{ year}^{-1}$ in C and NS plots, respectively (Table 1).

3.2 Net N Mineralization

Mean net N mineralization in the soil profile down to 50 cm measured in 1992 was 86 $\text{kg ha}^{-1} \text{ year}^{-1}$ and

115 kg ha⁻¹ year⁻¹ in C and NS plots, respectively. Most of the net N mineralization occurred in the FH and upper mineral soil to 20 cm depth (Fig. 1). In the L, 0–10 and 10–20 cm mineral soil layers net N mineralization was higher in NS plots than in C plots. In an acid forest soil subject to increased atmospheric nitrogen input, net mineralization rate ranged from 26 to 71 kg N ha⁻¹ year⁻¹ (Tietema et al., 1993) which is almost similar to our estimated values (Fig. 1). The mineralization rate found in C corresponds well with a similar site, Klosterhede (Persson et al., 2000). The rate in NS may have been overestimated. A repeated mineralization study in 1997 resulted in lower value, 97 kg ha⁻¹ year⁻¹ (Persson, Rudebeck, Karlsson, & Sjöberg, 2001).

Net nitrification could not be detected in the topsoil but occurred in the 10–50 cm layers in the mineral soil (Fig. 1). The potential nitrification (without roots) was higher in the NS (27 kg N ha⁻¹ year⁻¹) than in the C treatment (5 kg N ha⁻¹ year⁻¹). The higher amount of inorganic nitrogen as a result of N addition (see below) and low C/N ratio can explain the higher rate of nitrification and net mineralization in NS plots (Persson & Wirén, 1995).

3.3 Nitrogen Pools

The nitrogen pool of C and NS plots prior to treatment in needles was almost as much as in the stem, and branches together 172 and 180 kg N ha⁻¹, respectively. After six years treatment (1993) these values were 174 and 210 kg ha⁻¹, respectively

(Table 1). In NS plots the needle nitrogen pool exceeded the stem and branch pool by 25% in 1993 (302 and 376 kg ha⁻¹, respectively). The nitrogen pool in coarse roots was about 25% of that in stem and branches. The nitrogen pool in fine roots decreased by 30% from 1987 to 1993, from 71 to 48 kg ha⁻¹ in C plots and 57 kg ha⁻¹ in NS plots. Prior to treatment (1987) the total nitrogen pool in above and below ground biomass was 468 kg ha⁻¹. After 6 years treatment (1993) the total nitrogen pool in C and NS plots was 487 and 811 kg ha⁻¹, respectively. Thus, it increased by 4% in C plots and by 73% in NS plots.

The total N amount in the L-layer was significantly ($p < 0.05$) higher in NS than in C due to both higher N concentration and higher amount of litter, but there was no clear increase in the FH layer (Table 2). The total amount of N in L and FH layers was 959 and 1184 kg ha⁻¹ in C and NS, respectively. We assumed that there was no real change of total N in the mineral soil between the C and NS. The total amount of inorganic N in NS plots was significantly ($p < 0.05$) higher (38 kg ha⁻¹) than in C plots (Table 2).

The L and FH layers contained 225 kg ha⁻¹ more of total N in NS plots than in C plots (1184 vs. 959 kg ha⁻¹) indicating that there might have been an accumulation of total N by 38 kg ha⁻¹ year⁻¹ in NS during the 6-year period. Of the added inorganic N in NS, 47% was accumulated in above and below ground biomass and 37% in the soil. In contrast to our findings, Nadelhoffer, Downs, and Fry (1999) concluded that forest floor and mineral soils dominate

Fig. 1 Annual net N mineralization and potential nitrification (mean $\pm$ SE) as calculated from laboratory incubations in 1992, temperature and moisture corrections and soil pools in the field. Presence of net nitrification despite low net N mineralization (20–50 cm depth) is explained by nitrification of NH_4^+ present at the start of the incubation

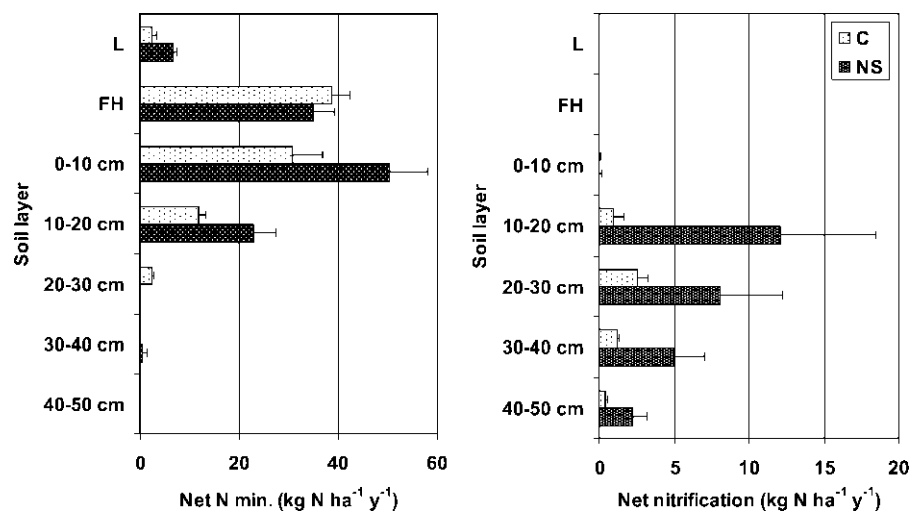


Table 2 Estimated mean ($\pm$ S.E.) amounts of inorganic nitrogen in 1992 and total N (kg ha^{-1}) in 1993 in different soil layers

Soil layer	Inorganic N (1992)		Total N (1993)	
	C	NS	C	NS
<i>L</i>	0.09 $\pm$ 0.01	0.3 $\pm$ 0.06	106 $\pm$ 18	308 $\pm$ 34
<i>FH</i>	21.6 $\pm$ 0.3	6.9 $\pm$ 0.7	853 $\pm$ 32	876 $\pm$ 68
Mineral soil (0–50 cm)	4.3 $\pm$ 0.8	31.0 $\pm$ 6.0	3000 $\pm$ 263	2860 $\pm$ 224
Total	6.0 $\pm$ 1.0	38.2 $\pm$ 6.4	3959 $\pm$ 274	4044 $\pm$ 287

Bold values indicate a significant increase ($p < 0.05$) between treatments within each layer

C control and NS ammonium sulphate

over trees as sinks for both ammonium and nitrate deposition rates, and measurements of forest ecosystem pools in a watershed showed that 70–92% of inputs in nitrogen-treated areas were retained in the soil pool (Magill et al., 1996).

According to Aber et al. (1989), in a N saturated stand, one can expect increased nitrification and acidification of the soil and enhanced losses of nitrate

nitrogen and aluminium by leaching and decreasing needle and fine-root biomass. During the study period, almost all these effects were found in the NS treatment, as nitrate-N leaching decreased fine root-biomass and soil acidification increased aluminium leaching (Bergholm, Berggren, & Alavi, 2003). There was no leaching of nitrate in C plots (Fig. 2a). However, a list of five characteristics classifying

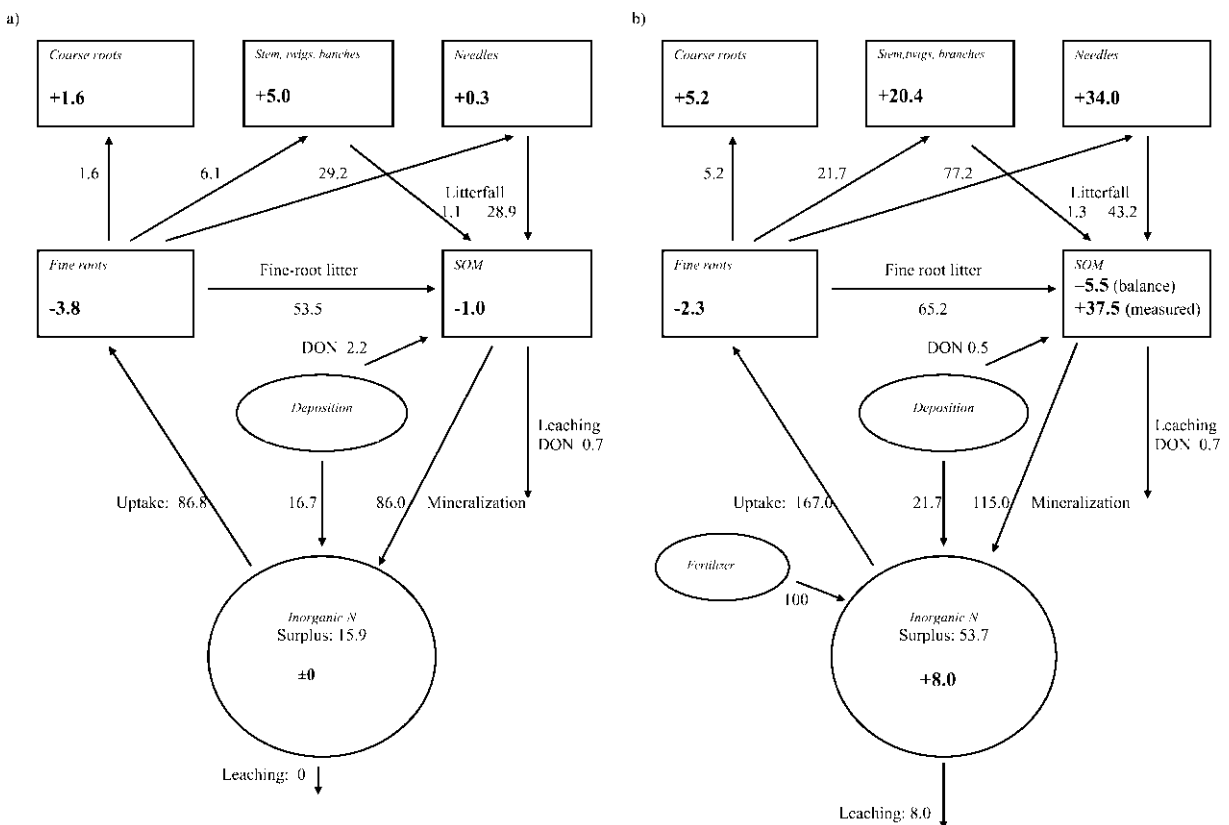


Fig. 2 Accumulation and fluxes of nitrogen ($\text{kg ha}^{-1} \text{ year}^{-1}$) in C **a** and NS **b** plots during 1988 to 1993. Values in *quadrats* and *circles* denote accumulation and *arrows* denotes fluxes.

(Data from Nilsson & Wiklund, 1992, 1994; Persson & Nilsson, 2000; Majdi & Kangas, 1997)

coniferous forest ecosystems as having low (N limited), intermediate or high N status (N saturated) (Gundersen, Schmidt, & Raulund-Rasmussen, 2006) showed that C plots belonged to the intermediate class in four of the five indicators. The NS plots belonged to the high N status class in two of the five, namely high input of N and high N concentration in needles. The remaining characteristics (C:N ratio of forest floor, the annual input of N via throughfall + litterfall and the proportion of input leached) belonged to the intermediate class in NS, indicating that NS was turning to a N saturated situation. The leached amount was 8% of the input which was (30–100%) lower than estimated for the high saturated class (Fig. 2b).

The balance calculation according to field measurements for the N pool in SOM in NS indicated a deficit of $5.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Fig. 2b). The figure may be underestimated due to overestimation of the mineralization rate. However, $38 \text{ kg ha}^{-1} \text{ year}^{-1}$ was accumulated in LFH (Table 2 and Fig. 2b), maybe by immobilisation of added N. In that case together with a lower mineralization rate, the missing amount would be $16 \text{ kg ha}^{-1} \text{ year}^{-1}$, with a similar amount as in C.

3.4 N Flux and Accumulation in Tree Components

During 1988–1993 the flux of N via roots to the above-ground biomass was estimated to be about 37 and $104 \text{ kg ha}^{-1} \text{ year}^{-1}$ in the C and NS plots, respectively, in which the needle biomass in C and NS plots received about 29 and $77 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively (Fig. 2a and b). Nitrogen was not accumulated in the C needle biomass. Magill et al. (1996) showed the higher foliar N concentration in N treated plots than in the control plots. The amount taken up by the needle biomass in C plots was recycled by litterfall to the forest floor (Fig. 2a). The recycled amount made up 79% of the net uptake by coarse roots and above ground biomass which fit well with a Finnish study (75%) by Finér, Mannerkoski, Piirainen, and Starr (2003). In contrast, $34 \text{ kg N ha}^{-1} \text{ year}^{-1}$ was accumulated in the NS needle biomass, mainly due to an enhanced N concentration in the needles, which was the main reason to the higher flux of N by needle litterfall in NS compared to that in C, 43 and $29 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively. The recycling by litterfall accounted for a minor part of the uptake in coarse root and above

ground biomass (43%) in NS. Nadelhoffer et al., (1999) suggested that the importance of trees as sinks for N inputs increases with N deposition rates.

N fluxes in C plots via fine-root litter production were higher ($54 \text{ kg ha}^{-1} \text{ year}^{-1}$) than that via needle litterfall ($29 \text{ kg ha}^{-1} \text{ year}^{-1}$). Corresponding fluxes in the NS plots were 65 and $43 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively. N transfer to coarse roots in C and NS plots was estimated to be 1.6 and $5.2 \text{ kg ha}^{-1} \text{ year}^{-1}$.

Our budget showed that the main proportion of added N in NS plots was accumulated in the tree biomass (47%). In contrast to our investigation, studies conducted in Harvard Forest, using ^{15}N traces (Nadelhoffer, Colman, Currie, Magill, & Aber, 2004; Nadelhoffer et al., 1999) indicated that soil was a stronger sink than tree biomass for ammonium and for nitrate inputs.

The N fluxes to the soil via root and needle litter as soil organic matter in NS treatment was together $110 \text{ kg ha}^{-1} \text{ year}^{-1}$ while net N-mineralization was $115 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Fig. 2b). The corresponding values for C plots were 83 and $86 \text{ kg ha}^{-1} \text{ year}^{-1}$. Putting together the inputs and outputs, we found that 12 and $51 \text{ kg ha}^{-1} \text{ year}^{-1}$ by taking into account the accumulated amount in SOM, $13 \text{ kg ha}^{-1} \text{ year}^{-1}$ was missing in both C and NS plots, respectively. This can be partly explained by bias in measured fluxes and mineralization rate. In a forest ecosystem study Magill et al. (1997) explained a very high amount of N missing in their budget as they only estimated fine root biomass without measuring root turnover. For more accurate partitioning of N inputs among forest components it is suggested to use ^{15}N measurements to trace recoveries of N input to the forest ecosystems (Nadelhoffer et al., 2004; Nadelhoffer et al., 1999; Nadelhoffer et al., 1995).

At 50 cm depth in NS plots $8 \text{ kg ha}^{-1} \text{ year}^{-1}$ inorganic N was leached with no leaching from C plots (Fig. 2). The annual loss of inorganic N from the NS plots increased gradually from $<0.01 \text{ kg}$ in 1988 to about 11 kg ha^{-1} in 1993 (data not shown). From the presented N budget, it can be concluded that fine root litter and litterfall play an important role in the cycling of N.

Our results suggest that net N-mineralization is promoted by addition of N in the soil and despite a high N uptake by spruce trees the losses of N in litterfall and fine root litter results in an incorporation of N in soil organic matter.

Acknowledgements This work was carried out within the Skogaby project financed by the Swedish Environmental Protection Agency (NV), the Foundation for Forest Research and the Foundation for Swedish Plant nitrogen Research. L.-O. Nilsson is acknowledged for providing data on nitrogen accumulation in trees. We would like to thank Ulf Johansson and the staff at the forest experimental station at Tönnersjöheden for providing excellent fieldwork. We are grateful to Tomas Grönqvist for comprehensive work with all chemical analyses.

References

- Aber, J., Nadelhoffer, K. J., Steudler, P., & Melillo, J. M. (1989). Nitrogen saturation in northern forest ecosystems. *Bioscience*, 39(6), 378–386.
- Ågren, G. I., Bosatta, E., & Magill, A. M. (2001). Combining theory and experiment to understand effects of inorganic nitrogen on litter decomposition. *Ecologia*, 128, 4–98.
- Bergholm, J., Berggren, D., & Alavi, G. (2003). Soil acidification induced by ammonium sulphate addition in a Norway spruce forest in Southwest Sweden. *Water, Air, and Soil Pollution*, 148, 87–109.
- Bergholm, J., Jansson, P.-E., Johansson, U., Majdi, H., Nilsson, L.-O., Persson, H., et al. (1995). Air pollution, tree vitality and forest production – The Skogaby project – General description of a field experiment with Norway spruce in South Sweden. In L.-O. Nilsson, R. F. Hüttl, U. T. Johansson & P. Mathy (Eds.), *Proceedings of a symposium on nitrogen uptake and cycling in forest ecosystem*, Halmstad, Sweden 7–10 June 1993. Ecosystem Research Report, 21, 69–87.
- Falkengren-Grerup, U. (1987). Long-term changes in pH of forest soils in southern Sweden. *Environmental Pollution*, 43, 79–90.
- FAO-Unesco (1990). Soil Map of the World.
- Finér, L., Mannerkoski, H., Piirainen, S., & Starr, M. (2003). Carbon and nitrogen pools in an old-growth, Norway spruce mixed forest in eastern Finland and changes associated with clear-cutting. *Forest Ecology and Management*, 174(1/3), 51–63.
- Gundersen, P., Schmidt, I. K., & Raulund-Rasmussen, K. (2006). Leaching of nitrate from temperate forests – effects of air pollution and forest management. *Environmental Review*, 14, 1–57.
- Hallbäck, L., & Tamm, C. O. (1986). Changes in soil acidity from 1927 to 1982–1984 in a forest area of South-west Sweden. *Scandinavian Journal of Forest Research*, 1, 219–232.
- Hedin, L. O., Granat, L., Likens, G., Buishand, T. A., Galloway, J. N., Butler, T. J., et al. (1994). Steep decline in atmospheric base cations in regions of European and North America. *Nature*, 367, 351–354.
- Jansson, P.-E. (1998). Simulation Model for Soil Water and Heat Conditions. Description of the SOIL Model' Swedish University of Agricultural Sciences, Dept. of Soil Science, Division of Agricultural Hydrotechnics, Uppsala, p 81.
- Magill, A. H., Aber, J. D., Berntson, G. M., McDowell, W. H., Nadelhoffer, K. J., Melillo, J. M., et al. (2000). Long-term nitrogen additions and nitrogen saturation in two temperate forests. *Ecosystems*.
- Magill, A. H., Aber, J. D., Currie, W. S., Nadelhoffer, K. J., Martin, M. E., McDowell, H., et al. (2004). Ecosystem response to 15 years of chronic nitrogen additions at the Harvard Forest LTER, Massachusetts, USA. *Forest Ecology and Management*, 196, 7–28.
- Magill, A. H., Aber, J. D., Hendricks, J. J., Bowden, R. D., Melillo, J. M., & Steudler, P. A. (1997). Biochemical response of forest ecosystems to simulated chronic nitrogen deposition. *Ecological Applications*, 7(2), 402–415.
- Magill, A. H., Downs, M. R., Nadelhoffer, K. J., Hallett, R. A., & Aber, J. D. (1996). Forest ecosystem response to four years of chronic nitrate and sulphate additions at Bear Brooks Watershed, Maine, USA. *Forest Ecology and Management*, 84, 29–37.
- Majdi, H. (1996). Root sampling methods – applications and limitations of minirhizotron technique. *Plant and Soil*, 185 (2), 225–258.
- Majdi, H., Damm, E., & Nylund, J. E. (2001). Longevity of mycorrhizal roots in relation to branching order and nutrient availability. *New Phytologist*, 150, 195–202.
- Majdi, H., & Kangas, P. (1997). Demography of fine roots in response to nutrient applications in a Norway spruce stand in southwestern Sweden. *Ecoscience*, 4, 199–205.
- Majdi, H., & Persson, H. (1995). Effects of ammonium sulphate application on the chemistry of bulk soil, rhizosphere, fine roots and fine-root distribution in a *Picea abies* (L.) Karst. Stand. *Plant and Soil*, 168–169, 159–160.
- Marklund, L. G. (1987). Biomass functions for Norway spruce (*Picea abies* (L.) Karst.)' (in Sweden). Department of Forest Survey, Report 43, Swedish University of Agricultural Sciences.
- Marklund, L. G. (1988). Biomass functions for pine, spruce and birch in Sweden. Department of Forest Survey, Report 45, Swedish University of Agricultural Sciences (in Swedish with English summary).
- Nadelhoffer, J. K., Colman, B. P., Currie, W. S., Magill, A., & Aber, J. D. (2004). Decadal-scale fates of ^{15}N tracers added to oak and pine stands under ambient and elevated N inputs at the Harvard Forest (USA). *Forest Ecology and Management*, 196, 89–107.
- Nadelhoffer, J. K., Downs, M. R., & Fry, B. (1999). Sinks for ^{15}N -enriched additions to an oak forest and a red pine plantation. *Ecological Applications*, 9, 72–86.
- Nadelhoffer, J. K., Downs, M. R., Fry, B., Aber, J. D., Magill, A. H., & Melillo, J. M. (1995). The fate of ^{15}N -labelled nitrate additions to a northern hardwood forest in eastern Maine, USA. *Oecologia*, 103, 292–301.
- Nihlgård, B. (1985). The ammonium hypothesis – An additional explanation to the forest dieback in Europe. *Ambio*, 14, 2–8.
- Nilsson, L.-O., & Wiklund, K. (1992). Influence of nitrogen and water stress on Norway spruce production in south Sweden – The role of air pollution. *Plant and Soil*, 147, 251–265.
- Nilsson, L.-O., & Wiklund, K. (1994). Nitrogen uptake in a Norway spruce stand following ammonium sulphate application, fertigation, irrigation, drought and nitrogen-free fertilisation. *Plant and Soil*, 164, 221–229.
- Persson, T., & Nilsson, L.-O. (2000). Skogabyförsök – effekter av långvarig kväve-och svaveltillförsel till ett skogsekosystem. *Naturvårdsverket*, Rapport 5173 (In Swedish).

- Persson, T., Rudebeck, A., Jussy, J. H., Colin-Belgrand, M., Priemé, A., Dambrine, E., et al. (2000). Soil nitrogen turnover – Mineralisation, nitrification and denitrification in european forest soils. In E.-D. Schulze (Ed.), *Carbon and nitrogen cycling in European forest ecosystems. Ecological Studies*, 142.
- Persson, T., Rudebeck, A., Karlsson, P., & Sjöberg, M. (2001). Kväve mineralisering och nitrifikation i Skogaby' Persson, T. and Nilsson, L.-O. (eds) in Skogabyförsöket – Effekter av långvarig kväve- och svaveltillförsel till ett skogsekosystem. Naturvårdsverket Rapport 5173 (summary in english).
- Persson, T., & Wirén, A. (1995). Nitrogen mineralization and potential nitrification at different depths in acid forest soils. *Plant and Soil*, 168–169, 55–66.
- SAS Institute Inc. (2002). *User's guide': Statistics, version 8.02 edition*. Cary, NC: SAS Institute Inc.
- Tamm, C. O. (1991). Nitrogen in terrestrial ecosystems: Questions of productivity, vegetational change, and ecosystem stability. *Ecological Studies*, 81, 115.
- Tietema, A., Riemer, J. M., Verstraten, M. P. van der Maas, M. P., van Wijk, A. J., & van Voorthuyzen, I. (1993). Nitrogen cycling in acid soils subject to increased atmospheric nitrogen input. *Forest Ecology and Management*, 57, 29–44.
- Viro, P. J. (1952). On the determination of stoniness. *Communicationes Instituti Forestalis Fenniae*, 40(3), 1–23 (in Finnish with English summary).
- Wright, R. E., & Rasmussen, L. (1998). Introduction to the NITREX and EXMAN projects. *Forest Ecology and Management*, 101, 1–7.

Modification of Soil Solid Aluminium Phases During an Extreme Experimental Acidification of A Horizons of Forest Soils from Southwest Europe

J. C. Nóvoa-Muñoz · E. García-Rodeja Gayoso

Received: 13 June 2005 / Accepted: 23 June 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Four umbric A horizons from acid forest soils were acidified in a batch type experiment and its effect in the Al pools of the solid phase analysed by means of selective dissolution methods. The results showed that Al release accounted for the consumption of 85–99% of the added protons, and causes a decrease of 2–33% of the ‘reactive’ Al pool of the soil solid phase. In these A horizons, inorganic non-crystalline Al and high stability Al-humus complexes are the main sources of the dissolved Al. The contribution of the complexes with intermediate stability only was relevant in the more acid horizon developed from phyllites (P18-A). The increase of equilibration time from 96 to 720 h did not caused significant differences in the decrease of the ‘reactive’ Al pool suggesting the acid neutralising reactions

occurred in less than 96 h. In most cases the quantity of released Al is in agreement with the decrease of the different reactive Al pools of the solid phase.

Keywords soil acidification · acid buffering mechanisms · umbric horizons · “active” Al · Al-humus complexes

1 Introduction

The dissolution of Al from different soil components is the main acid neutralising mechanism in acid forest soils (Berggren, Mulder, & Westerhof, 1998; Mulder, Van Breemen, & Eijck, 1989). The nature of each potential source of Al together to its abundance and its dissolution rate are the main factors determining its role in acid neutralisation when the soils are subjected to acid deposition (Wesselink, Van Breemen, Mulder, & Janssen, 1996).

The Al in humus complexes and the inorganic non-crystalline Al are the Al fractions that contribute most to the neutralisation of acid loads in podzolic (Berggren et al., 1998; Mulder et al., 1989; Van der Salm, Westerveld, & Verstraten, 2000; Zysset, Blaser, Luster, & Gehring, 1999) and other acid soils like andosols (Dahlgren & Saigusa, 1994) or acrisols (Zhu, Jiang, & Ji, 2004). Nevertheless, there is less information on the role of the different Al-humus pools and of the Al fractions with low dissolution rates in the neutralisation of acid loads.

J. C. Nóvoa-Muñoz (✉)
Área de Edafoloxía, Dpto. Bioloxía Vexetal e Ciencias do Solo, Facultade de Ciencias de Ourense,
Universidade de Vigo, Ourense, Spain
e-mail: edjuanca@uvigo.es

E. García-Rodeja Gayoso
Dpto. Edafoloxía e Química Agrícola, Facultade de Bioloxía, Universidade de Santiago de Compostela,
Santiago de Compostela, Spain

J. C. Nóvoa-Muñoz
Área de Edafoloxía. Fac. de Ciencias.
Universidade de Vigo. As Lagoas s/n,
32004 Ourense, Spain

The purpose of this work is to study the changes in different Al pools in the soil solid phase of four A horizons subjected to an extreme experimental acidification.

2 Materials and Methods

2.1 Study Area and Soil Characterization

The study was carried out using representative soils of the area surrounding a coal-fired power plant (1,400 MW) located at the north of Galicia (As Pontes, NW of Spain). Several sub samples of four A horizons from forest soils developed from different parent materials were collected and thoroughly mixed to obtain a composite sample for analysis. Soil samples are coded P11-A, P15-A, P18-A and C24-A hereafter. Prior to analysis, soil samples were air dried and passed through a 2-mm sieve. Soil pH was measured in water and in 0.01 M KCl (1:2.5, w/v ratio). Soil organic C was determined using a LECO analyzer. Effective cation exchange capacity (eCEC) was calculated as the sum of base cations (BC) extracted with 1 M NH_4Cl (5:100, w/v) and Al extracted with 1 M KCl (Al_K) (1:10, w/v). Aluminium in soil solid phase was extracted using 0.33 M LaCl_3 (Al_La), 0.5 M CuCl_2 (Al_Cu) and 0.2 M acid ammonium oxalate pH 3 (Al_o), following the methodology described by García-Rodeja, Nóvoa Muñoz, Pontevedra Pombal, Martínez Cortizas, and Buurman (2004). Thus, the pool of active Al in the soil was operatively separated into inorganic non-crystalline Al plus high stability Al-humus complexes (Al_ioa , Al_o - Al_Cu), moderate stability

Al-humus complexes (Al_om , Al_Cu - Al_La) and low-stability complexes (Al_ob , Al_La - Al_K).

2.2 Experimental Acidification

Five grams of air dried soil samples (<2 mm) were weighted in a centrifuge tube and 50 ml of different HCl solutions were added. The HCl solutions had a constant ionic strength of 0.010 M, adjusted with NaCl, and a proton load from ca. 0 to 30 $\text{cmol H}^+ \text{kg}^{-1}$ of soil (pH range from 5.6 to 1.5). All experiments were carried out in triplicate. The soil suspensions were shaken for 1 h and allowed to stand for 96 or 720 h. After centrifuging (15 min; 1,200 g), pH was determined and Al, K, Ca, and Mg were analysed by flame-AAS in filtered (0.45 μm) extracts.

Replicates of the acidified soil residues were collected to make a composite sample for each acid load and equilibration time (96 and 720 h). These soil residues were extracted, in duplicate, using the same solutions above mentioned which allowed us to estimate the changes induced by the experimental acidification in the Al pools defined in Section 2.1

3 Results and Discussion

The studied horizons are umbric A horizons from acid forest soils classified as Umbrisols (FAO, 1998), although P18 has properties close to podzolic soils. All are acid (pH-KCl < 4.2), organic matter rich and with Al as the dominant cation in the exchange complex (Table 1). The content in non crystalline Al (Al_o) ranged from 0.4 to 1.6% although Al-humus complexes were the dominant fraction of the 'reactive'

Table 1 Values of pH, total carbon, cation exchange complex and Al distribution in the studied soils

Soil horizon	Depth (cm)	Parent material	pH (H_2O)	pH (KCl)	C (%)	BC	eCEC	— $\text{cmol}_\text{c} \text{kg}^{-1}$ —			
								Al_K	Al_ob	Al_om	Al_ioa
P11-A	0–25	Amphibolite	5.31	4.51	7.7	2.0	2.9	0.9	2.9	36.6	137.6
P15-A	0–10	Granite	4.57	3.95	11.2	0.9	3.9	3.0	5.3	43.5	49.2
P18-A	0–10	Phyllite	3.36	3.01	14.5	6.8	15.1	8.3	3.9	9.6	18.2
C24-A	0–10	Schist	4.47	4.18	8.6	1.4	2.9	1.5	3.1	31.8	84.6

BC sum of base cations (Na + K + Ca + Mg), eCEC effective cation exchange capacity (BC + Al_K)

Al_ob and Al_om low- and moderate-stability Al-humus complexes, Al_ioa inorganic non-crystalline Al plus high stability Al-humus complexes.

Al pool. The contents of high- and moderate-stability Al-humus complexes are very close in all cases, representing from 31–54% and 30–47% of Al in complexes with organic matter (Table 1).

3.1 Base Cations and Aluminium Release

The quantity of base cations released as a consequence of the experimental acidification ($0.6\text{--}2.7\text{ cmol}_c\text{ kg}^{-1}$ of soil), was similar for both equilibrium times (96 and 720 h), and reflected their distribution in the exchange complex. They represented from 78 to 98% of the exchangeable pool, a proportion close to that obtained in previous studies on the acidification of forest soils from Galicia (Merino, Macías, & García-Rodeja, 1998).

Aluminium release represented 85–99% of proton consumption during the experimental soil acidification. Values close to 100% have been reported in different studies on the acidification of podzolic soils (i.e. Berggren et al., 1998). In the studied A horizons,

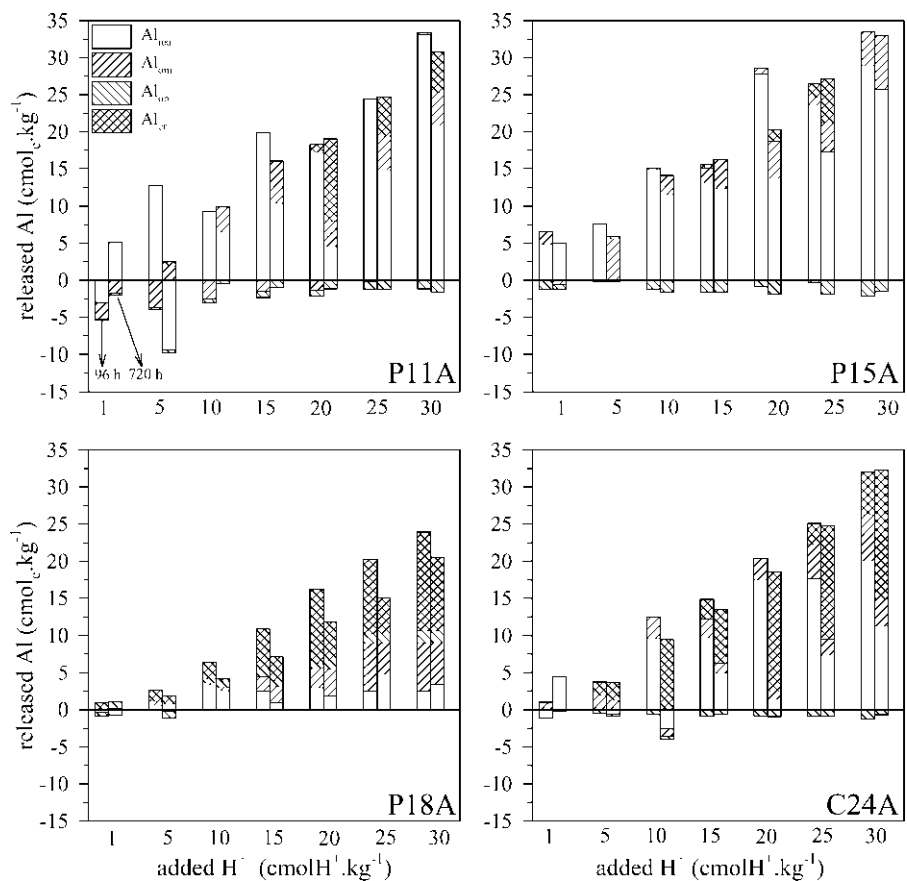
the increase of equilibration time from 96 to 720 h did not produced significant differences in the quantity of released Al.

3.2 Effects of Acidification on the Distribution of Al in the Solid Phase

In Fig. 1, where the contribution of the solid Al-phases to Al release during the experimental acidification is represented, positive values indicate the contribution of each soil Al pool to the Al measured in the equilibrium solution using the values of the 0 acid load as reference. Negative values are interpreted as a relative enrichment of a given Al pool. The difference between the Al measured in the equilibrium solution and the Al furnished by the dissolution of the reactive Al pools is assumed to be non-oxalate-extractable Al (Al_{cr}), being mineral weathering reactions one of their possible sources.

In the A horizons of the soil from amphibolites (P11-A), granite (P15-A) and schist (C24-A), the

Fig. 1 Contribution of soil solid Al-phases to Al release during the experimental acidification of A horizons after 96 (left bar) or 720 (right bar) hours of equilibration. Al_{ioa} : inorganic non-crystalline Al plus high stability Al-humus complexes ($\text{Al}_o\text{--Al}_{\text{Cu}}$); Al_{om} : Al in Al-humus with moderate stability; Al_{ob} : Al-humus in complexes with low stability; Al_{cr} : Al non-oxalate extractable Al



dissolution of Al from the inorganic non-crystalline Al and high stability Al-humus complexes pools (Al_{ioa}) are responsible of 63–100% of the released Al after 96 h of equilibrium (Fig. 1). On the contrary, in the P18-A horizon, from phyllites, this fraction only accounted for 11% (in the smaller acid load) to 23% (in the larger acid load) of the dissolved Al. Less than 20% of dissolved Al came from the dissolution of Al-humus complexes with intermediate stability (Al_{om}): 14–19% in C24-A and 4–14% in P15-A. In P18-A this fraction was the main source of released Al (16–62%). The Al-humus complexes with low stability (Al_{ob}) often showed a small relative increase although it never exceeded $2.5 \text{ cmol}_c \text{ kg}^{-1}$ (Fig. 1). However, in the P18-A horizon the Al_{ob} fraction contributed to 4–9% of the released Al.

For P11-A, P15-A and C24-A horizons, the good equivalence between dissolved Al and the quantities estimated from the changes in the reactive soil Al pools suggests that the contribution from non-oxalate extractable Al sources, such as crystalline Al or mineral weathering reactions, is negligible under the experimental conditions.

When the equilibrium time was increased until 720 h, the Al_{ioa} fraction remained as the main source of released Al in most of the studied horizons (Fig. 1) and acid loads. For this equilibrium time, the contribution of the Al_{om} fraction increased slightly in the horizons P11-A and P15-A (24–40%) whereas the role of Al_{cr} was more evident in C24-A but was less important in P18-A where it decreased to 31–55%.

The relative enrichment in the Al_{ioa} fraction showed by the P11-A and C24-A horizons is not significant as it only represents less than 0.1% of the reactive Al pool (Al_o). The decrease in the quantity of reactive Al in the studied horizons caused by the experimental acidification ranged from 2 to 33% of acid oxalate extractable Al. The similarity between the lost of reactive Al for the two equilibration times indicates that the acid neutralising reactions which involve the reactive Al pools of the soils took place in less than 96 h. Similar results have been reported by Van der Salm et al. (2000).

The decrease of the 'reactive' Al pool observed in these soils from Galicia is lower than those reported in other studies on soil acidification (Van der Salm et al., 2000; Zysset et al., 1999) where the loss of this Al fraction varied in the range 24–73%. Nevertheless, in all cases inorganic non-crystalline Al and high

stability Al-humus complexes were the main sources of dissolved Al in soils subjected to acid loads. This is the case of other soil acidification experiments performed in podzols (Berggren et al., 1998; Zysset et al., 1999), allophanic andosols (Dahlgren & Saigusa, 1994), acrisols (Zhu et al., 2004) and also in other soils from Galicia (Merino et al., 1998).

The preferential mobilisation of Al from inorganic non-crystalline components or from Al-humus complexes with high stability is still a matter of discussion. Lazerte and Findeis (1995) suggested that inorganic non-crystalline Al are more important than Al-humus complexes as sources of dissolved Al when the ratio $(Al_{oxalate} - Al_{pyrophosphate})/Al_{pyrophosphate}$ is over the 0.34–0.70 range. Following this hypothesis, the acidification of the studied horizons would imply the preferential dissolution of inorganic non-crystalline Al in P11-A and C24-A and of high stability Al-humus complexes in P15-A and P18-A. Nevertheless, our results suggest that both pools can act simultaneously as sources of dissolved Al. For Zhu et al. (2004), the inorganic non-crystalline Al pool acquires more relevance when the most reactive Al-humus complexes have been exhausted.

In this study, the contribution of the Al-humus complexes with intermediate stability (Al_{om}) is similar to the obtained by Merino et al. (1998) in other soils from Galicia. Recently, the important role of these complexes as a rapid source of dissolved Al in soils subjected to acidification has been reported in podzol Bs horizons (Van der Salm et al., 2000) and in acrisols (Zhu et al., 2004).

The relative enrichment in the Al_{ob} pool observed in some of the studied horizons (Fig. 1) had been previously reported by Mulder et al. (1989). They interpret that part of the dissolved Al can interact with the solid fraction increasing its content in exchangeable and weakly bonded to humus aluminium.

The contribution of non-oxalate-extractable Al to the released Al is very low ($<11 \text{ cmol}_c \text{ kg}^{-1}$) in P11-A and P15-A horizons but has more relevance in P18-A y C24-A. Some authors (Jersak & McColl, 1989) consider that the release of Al from crystalline phases only occurs after the complete dissolution of the 'reactive' Al pool. The results of this study suggests that these phases may contribute to dissolved Al when a fraction of the 'reactive' Al pool is still significant in the solid phase, as occurs in the P18-A horizon. This implies that, in some cases, a part of the Al

defined as ‘reactive’ can have a refractory behaviour and can not be dissolved in spite of the continuous increment of the acid load. The release of Al from crystalline mineral phases has also been reported in other soil acidification studies (Mulder et al., 1989; Van der Salm et al., 2000; Zysset et al., 1999).

The neutralising mechanism which lead to the Al release to the solution from Al-humus complexes is agree with the soil organic matter control of Al solubility showed in experimentally acidified A horizons of forest soils (Nóvoa-Muñoz, Martínez-Cortizas, & García-Rodeja, 2002). Under these conditions, the risk of Al toxicity is lower than those where dissolved Al is controlled by a hydroxi-Al phase (Adams, Hawke, Nilsson, & Powell, 2000). Thus, the attenuation of Al toxicity in A horizons is not only due to high concentration of Al-F species (Fernández, Álvarez, Fernandez & García-Rodeja, 1998), but also to the role of organic matter on Al activity.

4 Conclusions

The study of the effect of acid load on the Al fractionation of the solid phase of four A horizons of acid forest soils showed that the release of Al to the equilibrium solution is the main neutralising process. The amorphous inorganic Al pool and the Al-humus complexes with high stability appear as the main sources of the dissolved Al, followed by those with intermediate stability. The increase of the equilibration time from 96 to 720 h produces a more important contribution of crystalline mineral weathering to the dissolved Al.

Acknowledgements JCNM receives the support of a post-doctoral contract (Parga Pondal Programme) from Autonomous Government of Galicia (NW Spain).

References

Adams, M. L., Hawke, D. J., Nilsson, N. H. S., & Powell, K. J. (2000). The relationship between soil solution pH and

- Al³⁺ concentrations in a range of South Island (New Zealand) soils. *Australian Journal of Soil Research*, 38, 141–153.
- Berggren, D., Mulder, J., & Westerhof, R. (1998). Prolonged leaching of mineral forest soils with dilute HCl solutions: the solubility of Al and soil organic matter. *European Journal of Soil Science*, 49, 305–316.
- Dahlgren, R. A., & Saigusa, M. (1994). Al release rates from allophanic and nonallophanic andosols. *Soil Science and Plant Nutrition*, 40, 125–136.
- FAO (1998). *World reference base for soil resources. World soil resources report*, vol. 84. Rome: FAO.
- Fernández, M. J., Álvarez, E., Fernandez, V., & García-Rodeja, E. (1998). Chemistry of soil solutions under different kinds of vegetation in the vicinity of a thermal power station. *Environmental Pollution*, 101, 131–142.
- García-Rodeja, E., Nóvoa-Muñoz, J. C., Pontevedra Pombal, X., Martínez Cortizas, A., & Buurman, P. (2004). Aluminium fractionation through selective dissolution techniques in European volcanic soils. *Catena*, 56, 155–183.
- Jersak, J. M., & McColl, J. G. (1989). Aluminium release from solid-phase components of forest soil leached with citric acid. *Soil Science Society of America Journal*, 53, 550–555.
- Lazerte, B. D., & Findeis, J. (1995). The relative importance of oxalate and pyrophosphate extractable Al to the acidic leaching of Al in podzol B horizons from the Precambrian Shield, Ontario, Canada. *Canadian Journal of Soil Science*, 75, 43–54.
- Merino, A., Macías, F., & García-Rodeja, E. (1998). Aluminium dynamics in experimentally acidified soils from a humid-temperate region of South Europe. *Chemosphere*, 36, 1137–1142.
- Mulder, J., Van Breemen, N., Eijck, H. C. (1989). Depletion of soil aluminium by acid deposition and implications for acid neutralization. *Nature*, 337, 247–249.
- Nóvoa-Muñoz, J. C., Martínez-Cortizas, A., & García-Rodeja, E. (2002). *Influence of soil organic matter in Al solubility in acidified A horizons of acid forest soils of Galicia (NW Spain)*. BIOGEOMON. 4th International Symposium on Ecosystem Behaviour. Reading, UK.
- Van der Salm, C., Westerveld, J. W., & Verstraten, J. M. (2000). Release rates of Al from inorganic and organic compounds in a sandy podzol, during laboratory experiments. *Geoderma*, 96, 173–198.
- Wesselink, L. G., Van Breemen, N., Mulder, J., & Janssen, P. H. (1996). A simple model of soil organic matter complexation to predict the solubility of Al in acid forest soils. *European Journal of Soil Science*, 47, 373–384.
- Zhu, M., Jiang, X., & Ji, G. (2004). Experimental investigation on Al release from haplic acrisols in South-Eastern China. *Applied Geochemistry*, 19, 981–990.
- Zysset, M., Blaser, P., Luster, J., & Gehring, A. U. (1999). Aluminium solubility control in different horizons of a podzol. *Soil Science Society of America Journal*, 63, 1106–1115.

Exposure Programme on Atmospheric Corrosion Effects of Acidifying Pollutants in Tropical and Subtropical Climates

Johan Tidblad · Vladimir Kucera · Farid Samie ·
Surendra N. Das · Chalothorn Bhamornsut ·
Leong Chow Peng · King Lung So · Zhao Dawei ·
Le Thi Hong Lien · Hans Schollenberger ·
Chozi V. Lungu · David Simbi

Received: 17 June 2005 / Revised: 26 January 2006 / Accepted: 12 February 2006 / Published online: 6 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Many national exposure programmes have been performed in tropical and subtropical climates during the last 50 years. However, ambitious programmes involving more than a few countries are scarce. In this paper a recently formed network of test sites is described involving 12 test sites in Asia (India, Vietnam, Thailand, Malaysia and China including Hong Kong) and four test sites in Africa (South Africa, Zambia and Zimbabwe). This effort is part of the 2001–2004 Swedish International Development Agency (SIDA) funded Programme on Regional Air

Pollution in Developing Countries (RAPIDC). Corrosion attack after one (2002–2003) year of exposure (carbon steel, zinc, copper, limestone and paint coated steel) are presented together with environmental data (SO_2 , NO_2 , HNO_3 , O_3 , particles, amount and pH of precipitation, temperature and relative humidity) for all the test sites. The obtained corrosion values are substantially higher than expected for limestone, higher than expected for carbon steel and lower than expected for zinc compared to values calculated using the best available dose–response functions.

J. Tidblad (✉) · V. Kucera · F. Samie
Corrosion and Metals Research Institute,
Drottning Kristinas väg 48, 11428 Stockholm, Sweden
e-mail: johan.tidblad@kimad.com

S. N. Das
Regional Research Laboratory,
Bhubaneswar, India

C. Bhamornsut
Thailand Institute of Scientific and Technological Research,
Bangkok, Thailand

L. C. Peng
Malaysian Meteorological Service,
Kuala Lumpur, Malaysia

K. L. So
Hong Kong Environmental Protection Department,
Hong Kong, China

Z. Dawei
Chongqing Institute of Environmental
Science and Monitoring,
Chongqing, China

L. T. H. Lien
Institute of Materials Science,
Hanoi, Vietnam

H. Schollenberger
CSIR/Materials and Manufacturing,
Johannesburg, South Africa

C. V. Lungu
University of Zambia,
Lusaka, Zambia

D. Simbi
University of Zimbabwe,
Harare, Zimbabwe

Keywords air pollution · corrosion · carbon steel · zinc · copper · limestone · sub-tropics · tropics

1 Introduction

Atmospheric corrosion research in tropical and sub-tropical climates started around 1945 and results are available from several individual countries, for example Australia, Brazil, China, Cuba, India, Manila, New Zealand, Nigeria, Panama, Papua New Guinea, Philippine Islands, South Africa, Taiwan, Singapore and Vietnam (Tidblad, Mikhailov, & Kucera, 2000). However, ambitious programmes involving more than a few countries are limited to the MICAT project (Morcillo, Almeida, Rosales, et al., 1998) which includes 12 Ibero-American countries, Spain and Portugal, and the ISOCORRAG programme with more than 50 sites located in Europe, Argentina, Canada, Japan, New Zealand and USA (Knotkova, 1993). In Asia, the programme co-ordinated from Australia and involving 13 sites in Australia, Philippines, Thailand and Vietnam (Cole, 2000) and the programme co-ordinated from Japan and involving 23 sites in Japan, China, and South Korea (Maeda et al., 2001) should be mentioned. In Africa, the long-term study of Callaghan (1991) should not be left unnoticed. These programmes either have an environmental characterisation limited to SO₂ as a main pollutant (Callaghan, 1991; Knotkova, 1993; Morcillo et al., 1998) or have relatively short exposure times (Cole, 2000; Maeda et al., 2001).

Partly in order to fill this gap the present project “RAPIDC/Corrosion” was initiated as a part of the 2001–2004 Swedish International Development Co-operation Agency (SIDA) funded Programme on Regional Air Pollution in Developing Countries (RAPIDC). The Programme was managed on SIDA’s behalf by the Stockholm Environment Institute (SEI). The corrosion project was co-ordinated by the Swedish Corrosion Institute (SCI). The objective of the present paper is to describe the corrosion project and to give results and conclusions after 1 year of exposure. Results will in the future be available after 2 and 4 years of exposure. Since 1 year of exposure is a relatively short time it should be stressed that the conclusions presented in this paper are preliminary in anticipation of the results after 2 and 4 years.

Another important aspect of the project, which is not described here, was transfer of knowledge on establishing test sites, exposing specimens, collection of environmental data, and methodology of developing dose–response functions using modelling and statistical treatment.

2 Materials and Methods

2.1 Rack and Test Sites

Each site was maintained by a dedicated partner who was responsible for the safety of the rack, the exposure/withdrawal of passive samplers, the collection of environmental data and the withdrawal of corrosion specimens. After exposure, the samples were returned to the Swedish Corrosion Institute for evaluation of corrosion attack. Table 1 shows a list of test sites including the responsible organisations and starting date of exposure. The network of test sites consists of six partners (12 sites) in Asia and three partners (4 sites) in Africa.

At each test site a rack was erected supporting the materials samples and passive samplers (Fig. 1). The rack should preferably be situated in an open space, preferably on a roof, and it contains three distinct elements: (1) flat metal/painted samples (a–d) and their support consisting of a wooden frame; (2) stone samples and their support consisting of a carousel (e); (3) passive samplers and their support and sheltering consisting of two metal discs (f).

2.2 Characterisation of the Environment

Passive sampling was performed on all sites for the gaseous pollutants SO₂, NO₂, O₃ and HNO₃ (Ferm, De Santis, & Varotsos, 2005), and for particulate matter (Ferm, Watt, O’Hanlon, De Santis, & Varotsos, 2006). Sampling was performed on a bi-monthly basis i.e., samplers were exchanged each second month. The total sampling period was one year making in total six bi-monthly sampling periods. The starting date of the first sampling period varied from site to site and coincided with the starting date of the exposure of specimens given in Table 1. All exposure periods for passive samplers were consecutive so that the end of a sampling period marked the start of a new sampling period.

Table 1 List of test sites including country, responsible organisation and starting date of the exposure (year 2002)

Country	Test site name	Responsible organisation	Start
India	Bhubaneswar-u	Regional Research Laboratory	25 May
India	Bhubaneswar-r	Regional Research Laboratory	25 May
Thailand	Bangkok	Thailand Institute of Scientific and Technological Research	10 June
Thailand	Phrapradaeng	Thailand Institute of Scientific and Technological Research	11 June
Vietnam	Hanoi	Institute of Materials Science	23 July
Vietnam	Ho Chi Minh	Ho Chi Minh Branch of the Institute of Materials Science	26 July
Vietnam	Mytho	Ho Chi Minh Branch of the Institute of Materials Science	27 July
China	Chongqing	Chongqing Institute of Environmental Science and Monitoring	20 July
China	Tie Shan Ping	Chongqing Institute of Environmental Science and Monitoring	20 July
China	Hong Kong	Hong Kong Environmental Protection Department	18 July
Malaysia	Kuala Lumpur	Malaysian Meteorological Service	13 June
Malaysia	Tanah Rata	Malaysian Meteorological Service	14 June
South Africa	Johannesburg	CSIR / Materials and Manufacturing	21 August
Zambia	Kitwe	University of Zambia	27 August
Zambia	Magoye	University of Zambia	25 August
Zimbabwe	Harare	University of Zimbabwe	30 August

Complementary data on temperature, relative humidity, amount of rain and its pH were collected by the partners at a nearby environmental station. These data were reported to the Swedish Corrosion Institute on a monthly basis.

2.3 Sample Preparation and Evaluation of Corrosion Attack

For each of the materials and exposure periods, a set of three identical samples was prepared and exposed and these are referred to as the ‘triplicates.’ At each site a total of nine samples were exposed in the summer of 2002 for each material and this means that there are three sets of triplicates and that in total the samples are sufficient for three exposure periods. At present date withdrawals have been made after 1 and 2 years of exposure and a withdrawal after 4 years of exposure is planned in the summer of 2006. The samples exposed for 2 years are currently evaluated.

All flat samples, carbon steel (Dc 04, SS – EN 10 130), zinc (Z1 – DIN EN 1179), copper (Cu DHP, SS 5015) and painted steel were cut to dimensions $100 \times 150 \text{ mm}^2$ as suggested by ISO 9226. The thickness of all flat samples was 1 mm except for steel, which had a thickness of 2 mm. Carbon steel, zinc and copper were degreased and weighed prior to exposure. Steel was painted with two layers of alkyd (90 μm): (1) Conseal Primer 50 μm , fast drying alkyd based primer; (2) Ultra Topcoat 40 μm , quick drying and glossy acrylic



Fig. 1 Rack erected at a roof of a building in the urban site in Bhubaneswar: **a** carbon steel samples; **b** zinc samples; **c** copper samples; **d** painted steel samples; **e** limestone samples on a carousel; **f** passive samplers for gases and particulates fastened under circular discs for rain protection

modified alkyd topcoat and then edge protected using Vinyguard Silvergrey 88 from Jotun, Norway.

After exposure the visual impression of all flat samples was recorded by photography. The corrosion attack of the metal samples was evaluated with 10 min. consecutive pickling using Clarkes solution; 20 g Sb_2O_3 and 60 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 1,000 ml concentrated HCl ($\rho = 1.19 \text{ g ml}^{-1}$) for steel, 250 g glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and distilled water to make 1,000 ml, saturated solution for zinc and 50 g amidosulfonic acid (sulfamic acid) and distilled water to make 1,000 ml for copper. Painted steel was evaluated by visual examination of the spread of corrosion attack in both directions from the 1 mm cut but expressed as the average spread in one direction following ASTM D 1654-79a.

Portland limestone specimens of dimensions $50 \times 50 \times 8 \text{ mm}^3$ were obtained from the Building Research Establishment Ltd, United Kingdom, where also the corrosion attack was evaluated as mass change during exposure. The mass change was then recalculated to surface recession.

3 Results and Discussion

As mentioned in the introduction, 1 year of exposure is a relatively short time and therefore it is not

worthwhile at this stage to perform a detailed statistical analysis and development of dose–response functions. This analysis will be performed when data after 2 and 4 years of exposure are available. The focus is instead on presenting the data set and its characteristics and to make an estimate on the magnitude of the effects compared to those predicted by existing dose–response functions.

3.1 Environmental Data

The environmental data are given in Table 2. Compared to European values the values in Table 2 are similar except for temperature, amount of precipitation and SO_2 concentration, where the values are generally higher.

The SO_2 values are lower than $20 \mu\text{g m}^{-3}$ except for four extreme sites: Phrapradaeng, Chongqing, Tie Shan Ping and Kitwe. Worth noting is that the site Tie Shan Ping is a *rural* site situated close to Chongqing. The site Kitwe is located in the copper belt area in the northern part of Zambia. Other extreme sites worth mentioning are those in Malaysia: Kuala Lumpur and Tanah Rata. Kuala Lumpur has the highest HNO_3 values in the network probably due to a combination of the high NO_2 emissions, the high temperature, and the humid conditions. Tanah Rata is the cleanest site in the network. It has the same precipitation level as

Table 2 Environmental data including temperature (T), relative humidity (Rh), precipitation (Rain and pH), gaseous pollutants (HNO_3 , SO_2 , NO_2 and O_3) and particulate deposition (mass Cl^- , NO_3^- and SO_4^{2-})

Name	Temperature	Relative humidity	Rain	pH	HNO_3	SO_2	NO_2	O_3	mass	Cl^-	NO_3^-	SO_4^{2-}
Unit	$^{\circ}\text{C}$	%	mm		$\mu\text{g m}^{-3}$				$\mu\text{g cm}^{-2} \text{ month}^{-1}$			
Bhubaneswar–u	26.5	69	425	6.0	1.3	4	11	63	164	5.8	2.38	3.1
Bhubaneswar–r	26.5	69	425	6.0	1.0	3	5	63	70	1.7	1.02	1.4
Bangkok	29.3	76	1,371	6.8	2.3	11	39	38	35	0.3	2.18	1.6
Phrapradaeng	29.3	73	1,335	6.2	1.5	59	24	54	64	0.9	1.88	6.6
Hanoi	24.7	79	1,556	5.8	0.8	15	18	49	57	0.4	1.08	3.4
Ho Chi Minh	28.3	74	1,441	6.2	0.9	21	18	47	39	0.4	0.82	2.4
Mytho	27.0	81	1,222	6.4	0.3	2	9	36	62	2.9	0.62	1.3
Chongqing	18.5	70	1,162	4.5	1.3	99	45	52	162	0.7	1.46	18.5
Tie Shan Ping	18.5	90	1,133	4.2	1.8	51	10	71	61	0.2	1.25	7.2
Hong Kong	22.9	78	2,092	4.6	1.8	16	50	31	36	0.8	1.98	1.6
Kuala Lumpur	28.0	78	2,776	4.3	3.8	12	47	42	26	0.2	1.42	1.0
Tanah Rata	18.1	91	2,433	5.1	0.1	0	1	35	10	0.1	0.25	0.3
Johannesburg	17.2	78	417	4.8	2.1	18	28	51	21	0.1	0.62	0.7
Kitwe	22.6	58	1,083	4.7	0.9	92	11	72	64	0.2	0.52	6.5
Magoye	22.2	62	826	7.0	0.5	0	2	53	24	0.1	0.20	0.1
Harare	18.9	63	798	6.6	0.7	16	15	65	31	0.1	0.36	1.3

Kuala Lumpur but a much lower temperature and is situated in the Cameron highlands.

3.2 Corrosion Data

The corrosion data are given in Table 3. The analysis of painted steel and limestone are non-destructive while the analysis (pickling) of the metals are destructive and this is the reason why one of each of the triplicate metal samples (no. 3) have been saved for further analysis by other methods. As can be seen from Table 3 the difference between no. 1 and no. 2 for the metals is generally very low, in the range of 5%.

Regarding zinc one should note the slightly higher corrosion values for zinc at the Tie Shan Ping test site compared to Chongqing, which has a much higher SO_2 value, and also the very high values observed in Kitwe. For limestone, the high values in Johannesburg deserves to be mentioned, considering the pollution situation.

3.3 Correlation Between Environmental and Corrosion Data

Table 4 shows the rank correlations between the corrosion and selected environmental parameters. The

environmental parameter that has the highest correlation to most of the parameters is the amount of SO_4^{2-} analysed from the particulate deposited matter. It should be mentioned that SO_4^{2-} is not necessarily deposited as sulphate but may also be the reaction product of other particulate deposits, probably CaCO_3 , and gaseous SO_2 .

Other parameters with high correlation are SO_2 for carbon steel, pH for zinc and SO_2 , pH and HNO_3 for limestone. Nitric acid is a highly corrosive gas, even compared to SO_2 , as has been shown in recent laboratory experiments for copper (Samie, Tidblad, Kucera, & Leygraf, 2005).

3.4 Comparison of Observed and Predicted Data

Since it is not possible to develop dose–response functions based on the data presented in Table 2 and 3 due to the short exposure time it is instead worthwhile to use existing dose–response functions and compare the predicted values with the experimental values. Functions have recently been developed for the multi-pollutant situation within the EU 5FP project Model for multi-pollutant impact and assessment of threshold levels for cultural heritage (MULTI-ASSESS). These functions are also pre-

Table 3 Corrosion attack after 1 year of exposure (2002–2003) on painted steel (spread from cut), carbon steel, zinc and copper (mass loss) and limestone (surface recession)

Name	Painted steel			Carbon steel		Zinc		Copper		Limestone		
Unit	mm			g m^{-2}						μm		
Sample	No. 1	No. 2	No. 3	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 3
Bhubaneswar-u	0.6	0.6	0.7	157	157	4.2	4.3	8.4	8.1	13.2	14.3	12.5
Bhubaneswar-r	0.6	0.8	0.7	157	155	3.4	3.7	12.3	11.5	7.7	8.9	11.5
Bangkok	0.8	0.6	0.7	116	115	4.3	4.8	14.3	15.6	13.2	13.9	15.2
Phrapradaeng	0.6	0.5	0.6	280	282	5.5	5.9	16.8	17.4	28.9	3.0	17.3
Hanoi	1.0	1.4	1.1	181	182	5.9	6.2	5.5	5.2	23.1	5.4	21.8
Ho Chi Minh	0.8	0.9	0.8	162	165	6.4	7.3	7.7	8.3	5.3	7.6	7.1
Mytho	1.2	0.9	1.0	166	167	4.4	4.3	11.3	12.8	9.3	7.4	11.5
Chongqing	4.0	5.3	4.4	789	776	9.1	9.0	24.6	23.7	17.5	38.7	37.4
Tie Shan Ping	4.0	4.2	3.1	490	494	10.8	12.4	17.7	18.0	30.1	29.4	33.8
Hong Kong	0.7	0.7	0.7	148	153	6.4	6.4	6.6	6.8	18.2	17.8	18.5
Kuala Lumpur	0.7	0.7	0.6	139	139	7.8	8.4	9.2	9.9	22.9	21.0	20.9
Tanah Rata	0.7	0.6	0.7	49	52	7.3	7.7	10.2	10.8	10.1	19.3	9.4
Johannesburg	0.4	0.4	0.4	101	109	1.9	2.1	4.5	4.6	34.1	20.6	39.4
Kitwe	4.2	3.6	3.5	464	463	26.8	27.3	12.7	12.7	32.8	35.8	36.4
Magoye	1.1	0.4	0.5	25	28	1.9	2.0	4.7	5.4	8.4	8.8	7.8
Harare	0.5	0.4	0.6	194	192	3.4	3.5	4.2	3.9	8.8	8.1	8.1

sented in a paper within this special volume of Water, Air and Soil Pollution dedicated to the Acid Rain 2005 conference (Kucera et. al., 2005). However, due to the relatively high measured SO₂ levels it is more correct to use functions for the SO₂-dominating situation developed within the International co-operative programme on effects on materials including historic and cultural monuments (ICP Materials). Functions from this program are available for zinc, copper and limestone but not for carbon steel (Tidblad et al., 2001),

$$\begin{aligned} \text{ML}_{\text{Zn}} &= 1.4[\text{SO}_2]^{0.22} e^{0.018\text{Rh}-0.021(T-10)} + 0.029\text{Rain}[\text{H}^+] & T > 10^\circ\text{C} \\ \text{ML}_{\text{Cu}} &= 0.0027[\text{SO}_2]^{0.32}[\text{O}_3]^{0.79}\text{Rh} \cdot e^{-0.032(T-10)} 0.050\text{Rain}[\text{H}^+] & T > 10^\circ\text{C} \\ R_{\text{Limestone}} &= 2.7[\text{SO}_2]^{0.48} e^{-0.018T} + 0.019\text{Rain}[\text{H}^+] \end{aligned}$$

where ML is the mass loss after 1 year of exposure in g/m², R is the surface recession after 1 year of exposure in μm , [SO₂] is the SO₂ concentration in $\mu\text{g}/\text{m}^3$, [O₃] is the O₃ concentration in $\mu\text{g}/\text{m}^3$, Rh is the relative humidity in %, T is the temperature in °C, Rain is the amount of precipitation in mm/year and [H⁺] is the hydrogen ion concentration in precipitation in mg/l. For carbon steel a function developed within ISO TC 156 *Corrosion of metals and alloys* has been used (Mikhailov, Tidblad, & Kucera, 2004)

$$\begin{aligned} R_{\text{Steel}} &= 1.77(0.8[\text{SO}_2])^{0.52} e^{0.020\text{Rh}-0.054(T-10)} \\ &\quad + 0.102D_{\text{Cl}}^{0.62} e^{0.033\text{Rh}+0.040T} \\ &T > 10^\circ\text{C} \end{aligned}$$

where D_{Cl} is the chloride deposition in $\text{mg m}^{-2} \text{day}^{-1}$. The results of applying these functions are shown in Table 5 together with the observed values. The values are given in a common unit (μm) for all materials by

Table 4 Rank correlations between environmental (Table 2) and corrosion (Table 3) data

	SO ₄ ²⁻	SO ₂	HNO ₃	-pH
Paint coated steel	0.55	–	–	–
Carbon steel	0.85	0.74	–	–
Zinc ^a	0.52	–	–	0.68
Copper	0.62	–	–	–
Limestone ^b	0.62	0.58	0.60	0.80

^a Kitwe excluded; ^b Johannesburg excluded

Table 5 Lower and upper quartiles of observed and predicted values using RAPIDC environmental data and dose–response functions (see text) from other exposure programmes

	Observed	Predicted	R ²
Carbon steel	17–28 μm	9–22 μm	0.79
Zinc ^a	0.5–1.0 μm	0.7–1.3 μm	0.58
Copper	0.7–1.5 μm	0.5–1.1 μm	0.27
Limestone ^b	9–20 μm	3–10 μm	0.74

^a Kitwe excluded; ^b Johannesburg excluded

using the density of carbon steel (7.8 g cm⁻³), zinc (7.14 g cm⁻³) and copper (8.93 g cm⁻³). For carbon steel, copper and limestone the predicted values are lower but for zinc the observed values are lower. One explanation of the low zinc values can be that this material is particularly sensitive to the starting conditions of the exposure. It is worth noting the substantial difference between observed and predicted values for Portland limestone. For copper the comparison is misleading since the 1-year values cannot be predicted by the proposed equation ($R^2=0.27$). Therefore, the 2- and 4-year results will be very valuable in the assessment of corrosion rates in the RAPIDC network compared to results from other networks in Europe.

4 Conclusions

A network of organisations and corrosion test sites have been formed with six partners (12 sites) in Asia and three partners (4 sites) in Africa and an exposure programme was started in May–August 2002. Complete results of an extensive environmental characterisation and corrosion data of painted steel, carbon steel, zinc, copper and limestone after one year of exposure in the network have been presented and the conclusions below are preliminary in anticipation of results after 2 and 4 years of exposure. SO₂ pollution is the most decisive factor but in addition a correlation

to pH has been found for zinc and limestone and a correlation to HNO_3 has been found for limestone. Based on best available dose–response functions the corrosion values are higher than expected except for zinc where the values are lower than expected. For limestone the values are substantially higher than expected. For painted steel and copper 1 year of exposure is too short and a comparison can be misleading. Therefore, future studies will include a complete evaluation of the 2- and 4-year results that will be very valuable in the assessment of corrosion rates in the RAPIDC network compared to results from other networks in Europe.

Acknowledgement The Swedish International Development Cooperation Agency (SIDA) is acknowledged for financial support. We are also grateful to Martin Ferm of the IVL Swedish Environmental Research Institute for valuable discussions about the results of the passive samplers.

References

- Callaghan, B. G. (1991). Atmospheric corrosion testing in southern Africa: results of a twenty year national exposure programme. Division of Materials Science and Technology, GAcSir 450H6025*9101, Scientia Publishers, CSIR, pp. 75.
- Cole, I. S. (2000). Mechanisms of atmospheric corrosion in tropical environments. ASTM STP 1399. In S. W. Dean, G. Hernandez-Duque Delgadillo & J. B. Bushman (Eds.), *American Society for Testing and Materials*. West Conshohocken, PA.
- Ferm, M., De Santis, F., & Varotsos, C. (2005). Nitric acid measurements in connection with corrosion studies. *Atmospheric Environment*, 39, 6664–6672.
- Ferm, M., Watt, J., O'Hanlon, S., De Santis, F., & Varotsos, C. (2006). Deposition Measurement of Particulate Matter in connection with Corrosion Studies. *Analytical and Bio-analytical Chemistry*. (in press)
- Knotkova, D. (1993). Atmospheric corrosivity classification. Results of the international testing program ISOCOR-RAG," corrosion control for low-cost reliability. In: *12th international corrosion congress*, vol. 2 (pp. 561–568). Houston, Texas: Progress Industries Plant Operations, NACE International.
- Kucera, V., Tidblad, J., Kreislova, K., Knotkova, D., Faller, M., Reiss, D., et al., (2005). The UN/ECE ICP materials multi-pollutant exposure on effects on materials including historic and cultural monuments. *Acid Rain*. (in press)
- Maeda, Y., Morioka, J., Tsujino, Y., Satoh, Y., Xiaodan, Z., Mizoguchi, T., et al. (2001). Materials damage caused by acidic air pollution in East Asia. *Water, Air and Soil Pollution*, 130, 141–150.
- Mikhailov, A. A., Tidblad, J., & Kucera, V. (2004). The classification system of ISO 9223 standard and the dose–response functions assessing the corrosivity of outdoor atmospheres. *Protection of Metals*, 40(6), 541–550.
- Morcillo, M., Almeida, E. M., Rosales, B. M., et al. (Eds.) (1998). *Funciones de Dano (Dosis/Respuesta) de la Corrosion Atmosferica en Iberoamerica, Corrosion y Proteccion de Metales en las Atmosferas de Iberoamerica*, Programma CYTED, Madrid, Spain, pp. 629–660.
- Samie, F., Tidblad, J., Kucera, V., & Leygraf, C. (2005). Atmospheric corrosion effects of HNO_3 . Method development and initial results on laboratory exposed copper. *Atmospheric Environment*, 39/38, 7362–7373.
- Tidblad, J., Kucera, V., Mikhailov, A. A., Henriksen, J., Kreislova, K., Yates, T., et al. (2001). UN/ECE ICP Materials. Dose–response functions on dry and wet deposition effects after 8 years of exposure. *Water, Air and Soil Pollution*, 130, 1457–1462.
- Tidblad, J., Mikhailov, A., & Kucera, V. (2000). *Acid deposition effects on materials in subtropical and tropical climates. Data compilation and temperate climate comparison*. SCI Report 2000:8E, Swedish Corrosion Institute, Stockholm, Sweden.

UN/ECE ICP Materials Dose-response Functions for the Multi-pollutant Situation

Vladimir Kucera · Johan Tidblad · Katerina Kreislova ·
Dagmar Knotkova · Markus Faller · Daniel Reiss · Rolf Snethlage ·
Tim Yates · Jan Henriksen · Manfred Schreiner · Michael Melcher ·
Martin Ferm · Roger-Alexandre Lefèvre · Joanna Kobus

Received: 17 June 2005 / Revised: 26 January 2006 / Accepted: 12 February 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract A “multi-pollutant exposure programme” reflecting the new pollution situation where SO₂ is no longer the dominating pollutant has been performed by the International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) within the activities of the Convention on Long-range Trans-boundary Air Pollution. The main results obtained in the period 1997–2003 are summarised. Dose-response functions are presented for carbon steel, zinc, copper, bronze and limestone. Parameters involved in the functions include besides SO₂ and pH, which were included in the previously developed functions from

ICP Materials, also the effect of particulate matter and HNO₃.

Keywords air pollution · corrosion · materials · dose-response functions · HNO₃ · particulate matter

1 Introduction

Dose-response functions are an important tool for mapping areas of increased risk of corrosion and for calculating corrosion costs. In the past, several dose-response functions for individual materials have been

V. Kucera · J. Tidblad (✉)
Corrosion and Metals Research Institute, Drottning
Kristinas väg 48, SE 11428, Stockholm, Sweden
e-mail: johan.tidblad@kimab.com

K. Kreislova · D. Knotkova
SVUOM Ltd., Prague, Czech Republic

M. Faller · D. Reiss
EMPA – Corrosion and Materials Integrity,
Dübendorf, Switzerland

R. Snethlage
Bavarian State Department for Historical Monuments,
Munich, Germany

T. Yates
Building Research Establishment Ltd. (BRE),
Watford, United Kingdom

J. Henriksen
Norwegian Institute for Air Research (NILU),
Kjeller, Norway

M. Schreiner · M. Melcher
Academy of Fine Arts, Vienna, Austria

M. Ferm
Swedish Environmental Research Institute Ltd. (IVL),
Gothenburg, Sweden

R.-A. Lefèvre
LISA – Université Paris XII, Paris, France

J. Kobus
Institute of Precision Mechanics, Warsaw, Poland

proposed using results based on different exposure programmes, for example the NAPAP programme (Baedecker, 1990) and Scandinavian exposure programmes (Haagenrud & Henriksen, 1996). Common for the past exposure programmes and functions was the focus on the SO_2 concentration, which was the main corrosion stimulator. Therefore, all these functions should in principle be denoted “dose-response functions for the SO_2 dominating situation”. This era culminated with the development of dose-response functions from the International Co-operative Programme on Effects of Materials including Historic and Cultural Monuments (ICP Materials) using the 8-year results (1987–1994) and these were reported at Acid Rain 2000, Tsukuba, Japan (Tidblad et al., 2001).

In the recent decades the decreasing SO_2 levels and the increasing car traffic causing elevated levels of nitrogen compounds, ozone and particulates has created a new multi-pollutant situation in Europe where SO_2 no longer is dominant. This was recognised within ICP Materials already in 1996 and a year later the ICP Materials multi-pollutant exposure program started (1997–2001). This exposure was later complemented and extended with measurements of HNO_3 and particulate matter by the EU project Model for multi-pollutant impact and assessment of threshold levels for cultural heritage MULTI-ASSESS (Kucera et al., 2005). The present paper summarises the development of the new dose-response functions for the multi-pollutant situation based on data from the ICP Materials multi-pollutant exposure and the MULTI-ASSESS project.

2 Experimental

A Task Force is organising the programme originally with Sweden as lead country and the Swedish Corrosion Institute serving as the main research centre. Since January 2005 the Chairmanship of ICP Materials is shared between Sweden (Swedish Corrosion Institute) and Italy (ENEA). Sub-centres in different countries have been appointed, each responsible for their own group of materials. All environmental measurements are reported and compiled by the environmental sub-centre, the Norwegian Institute for Air Research (NILU). In each country a National contact person has been appointed responsible for the sub-centre and/or test sites.

2.1 Network of Test Sites

The network consists of 29 test sites from 18 countries (Table 1). Of the 39 sites included in the original network, 21 are kept in the multi-pollutant programme. In addition, new sites have been added and include urban sites in Paris, Berlin, Tel Aviv, London, Los Angeles and Antwerpen as well as rural sites in Svanvik, Norway and Chaumont, Switzerland. This means an increase of the share of urban sites from 14 of 39 to 16 of 29 and an increase of the number of involved countries from 14 to 19.

2.2 Characterisation of the Environment

At each site the measured environmental data (ICP Materials, 2003a) includes climatic parameters (temperature, relative humidity, time of wetness, and sunshine radiation), gaseous pollutants (SO_2 , NO_2 and O_3) and precipitation (total amount, conductivity and concentration of the ions H^+ , SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} and K^+). This data is in general not measured exclusively for ICP Materials but are instead collected from nearby environmental stations. For cost reasons a test site is preferably situated where high quality measurements are already made. Thus, the analytical methods and instruments used for measuring the environmental data may vary from site to site.

In addition to these parameters, HNO_3 and particulates (total mass and SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} and K^+) have been measured within the EU 5FP MULTI-ASSESS project at all test sites with the same methodology, which is completely new in the area of materials damage estimation, considering the large network of test sites. Besides the differences in test sites, this environmental characterisation is the main difference between the original 8-year exposure programme and the presently described multi-pollutant exposure program. These measurements were performed with passive samplers for HNO_3 (Ferm, De Santis, & Varotsos, 2005) and particulate matter (Ferm, Watt, O'Hanlon, De Santis, & Varotsos, 2006) that were validated within the MULTI-ASSESS project. The latter also involves a description of the correlation between the deposited PM and the measured PM10 concentration in the atmosphere of the test sites. Details of the measurement techniques

Table 1 List of test sites used in the multi-pollutant exposure programme showing number, name, country and type of atmosphere

No	Name	Country	Type
1	Prague-Letnany	Czech Republic	Urban
3	Kopisty	Czech Republic	Industrial
5	Ähtäri	Finland	Rural
7	Waldhof-Langenbrügge	Germany	Rural
9	Langenfeld-Reusrath	Germany	Rural
10	Bottrop	Germany	Industrial
13	Rome	Italy	Urban
14	Casaccia	Italy	Rural
15	Milan	Italy	Urban
16	Venice	Italy	Urban
21	Oslo	Norway	Urban
23	Birkenes	Norway	Rural
24	Stockholm South	Sweden	Urban
26	Aspvreten	Sweden	Rural
27	Lincoln Cathedral	United Kingdom	Urban
31	Madrid	Spain	Urban
33	Toledo	Spain	Rural
34	Moscow	Russian Federation	Urban
35	Lahemaa	Estonia	Rural
36	Lisbon	Portugal	Urban
37	Dorset	Canada	Rural
40	Paris	France	Urban
41	Berlin	Germany	Urban
43	Tel Aviv	Israel	Urban
44	Svanvik	Norway	Rural
45	Chaumont	Switzerland	Rural
46	London	United Kingdom	Urban
47	Los Angeles	USA	Urban
49	Antwerpen	Belgium	Urban

Sites 1–39 were also used in the original exposure programme and sites 40–49 are new test sites.

can be found in the mentioned papers, which are also summarised in the MULTI-ASSESS publishable final report (Kucera et al., 2005).

2.3 Materials and Evaluation of Corrosion Attack

Standard specimens of carbon steel, zinc, copper, bronze, limestone, paint coated steel, and glass representative of medieval stained glass windows have been exposed in unsheltered and for some materials sheltered position on racks. The evaluation of corrosion effects on materials is done by standardised or well-established procedures: carbon steel (ICP Materials, 2003b), zinc (ICP Materials, 2003c), copper and bronze (ICP Materials, 2003d), limestone (ICP Materials, 2003e), painted steel (ICP Materials, 2003f) and glass (ICP Materials, 2003g, 2004). Also,

evaluation of corrosion effects on materials is performed at dedicated sub-centres, each responsible for a material, or group of materials, and for performing all corrosion analyses of this material regardless of where it was exposed:

- SVUOM Ltd., Prague, Czech Republic, responsible for carbon steel
- EMPA, Corrosion/Surface Protection, Dübendorf, Switzerland, responsible for zinc
- Bavarian State Department of Historical Monuments, Munich, Germany responsible for copper and cast bronze.
- Building Research Establishment (BRE Ltd.), Garston, Watford, United Kingdom, responsible for Portland limestone.
- Norwegian Institute for Air Research (NILU), Lilleström, Norway responsible for painted steel.

- Institute of Chemistry, Academy of Fine Arts, Vienna, Austria responsible for glass materials representative of medieval stained glass windows.

3 Results and Discussion

Selected results of environmental and corrosion data are presented as bar graphs in Fig. 1, 2, and 3 giving annual values of temperature, relative humidity, precipitation, HNO_3 , SO_2 , particulate total deposition, and limestone, zinc and steel corrosion. Worth noting is the relatively high HNO_3 concentration in Paris in combination with the elevated corrosion levels for zinc and to a lesser extent limestone but not for steel at this site. This observation is also reflected in the developed dose-response functions described below where HNO_3 proved to be a significant parameter for limestone and zinc but not for the other materials.

3.1 Statistical Evaluation of Results

The statistical analysis is based on corrosion values of carbon steel, zinc, copper, bronze and limestone after 1, 2 and 4 years of exposure in the multi-pollutant programme. One important criterion for the developed dose-response functions is that they should be suitable for mapping areas with increased risk of corrosion. Therefore the environmental parameters have been restricted to those that are easily available and these are given in Table 2 together with the corrosion attack parameters, including abbreviations and units. For temperature a maximum of the corrosion effect of SO_2 is observed at about 9–11°C. The increasing part can be related to the increased time of wetness. The decreasing part is attributed to a faster evaporation of moisture layers e.g. after rain or dew periods and a surface temperature above the ambient temperature due to sun radiation which result in a decrease of the surface time of wetness (Tidblad et al., 2001). For relative humidity the transformed variable $\text{Rh}_{60} = (\text{Rh} - 60)$ when $\text{Rh} > 60$; otherwise 0 is frequently used in the dose-response functions. The new important parameter HNO_3 is not easily available but may be calculated from other easily available parameters i.e., temperature, relative humidity, NO_2 and O_3 (Kucera et al., 2005).

The statistical results presented here are the result of linear/non-linear regression. Other techniques for producing regression functions have also been tested and these give in some cases better results but may involve combination of terms that are difficult to justify based on physical/chemical arguments. The result of the analysis is summarised in Table 3.

The climatic parameters (T, Rh and Rain) are all included in almost all of the functions. Both pH and SO_2 are included in all of the functions and these parameters were also present in the dose-response functions developed previously. NO_2 is not included in any of the functions directly but as will be seen below it is closely related to the HNO_3 concentration. The remaining parameters are included as an additional contribution depending on material. The effects of HNO_3 (zinc and limestone) and PM (carbon steel, bronze and limestone) are new. In the following the functions for the individual materials will be presented briefly.

3.2 Dose-response Functions

3.2.1 Carbon Steel

No previous dose-response function exists from the 8-year ICP Materials exposure programme. However, a recently developed function based on work within ISO TC 156/WG4 with the aim of future revision of ISO 9223 resulted in the following equation describing the corrosion attack after 1 year of exposure

$$r_{\text{corr}} = 1.77[\text{SO}_2]^{0.52} e^{0.020\text{Rh}} e^{f(T)} + g(\text{Cl}^-, \text{Rh}, T)$$

where r_{corr} is measured in μm , $f(T) = 0.15(T - 10)$ when $T < 10^\circ\text{C}$; otherwise $-0.054(T - 10)$, and $g(\text{Cl}^-, \text{Rh}, T)$ is a function describing the effect of dry deposition of chloride in combination with relative humidity and temperature. The temperature interval used in the derivation of this function was from -20 to $+30^\circ\text{C}$ while the multi-pollutant database only includes values from 0 to $+25^\circ\text{C}$. Since the multi-pollutant data set did not disagree with this temperature function it was used in the resulting multi-assess function

$$\text{ML} = 29.1 + t^{0.6} \left(21.7 + 1.39[\text{SO}_2]^{0.6} \text{Rh}_{60} e^{f(T)} + 1.29\text{Rain}[\text{H}^+] + 0.593\text{PM}_{10} \right)$$

Fig. 1 Amount of precipitation (*top*), relative humidity (*middle*) and temperature (*bottom*) data for the multi-pollutant exposure (1997–2001)

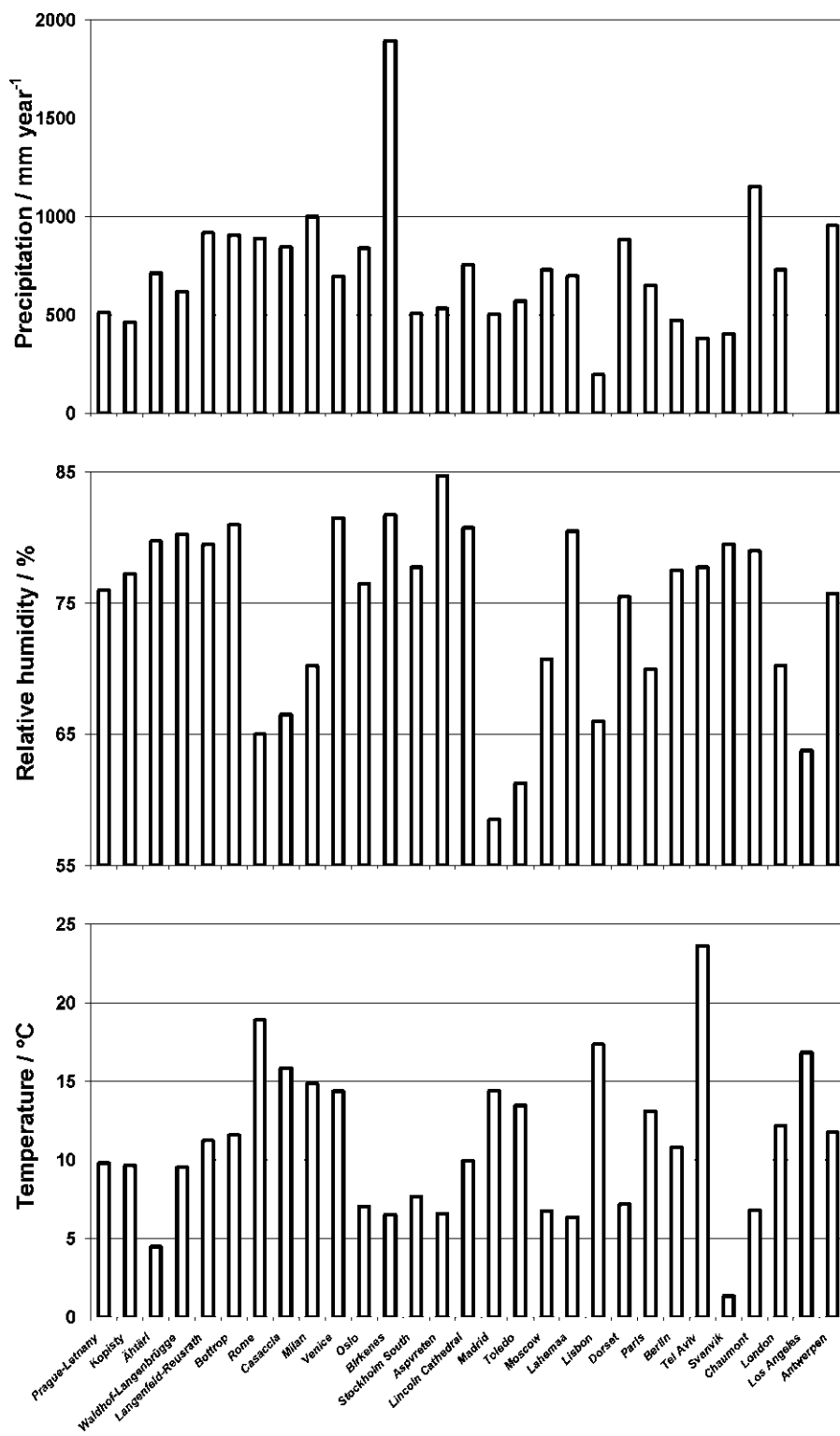


Fig. 2 Particulate deposition (*top*), SO_2 (*middle*) and HNO_3 (*bottom*) data for the multi-pollutant exposure (2002–2003 for particulate deposition and HNO_3 , 1997–2001 for SO_2)

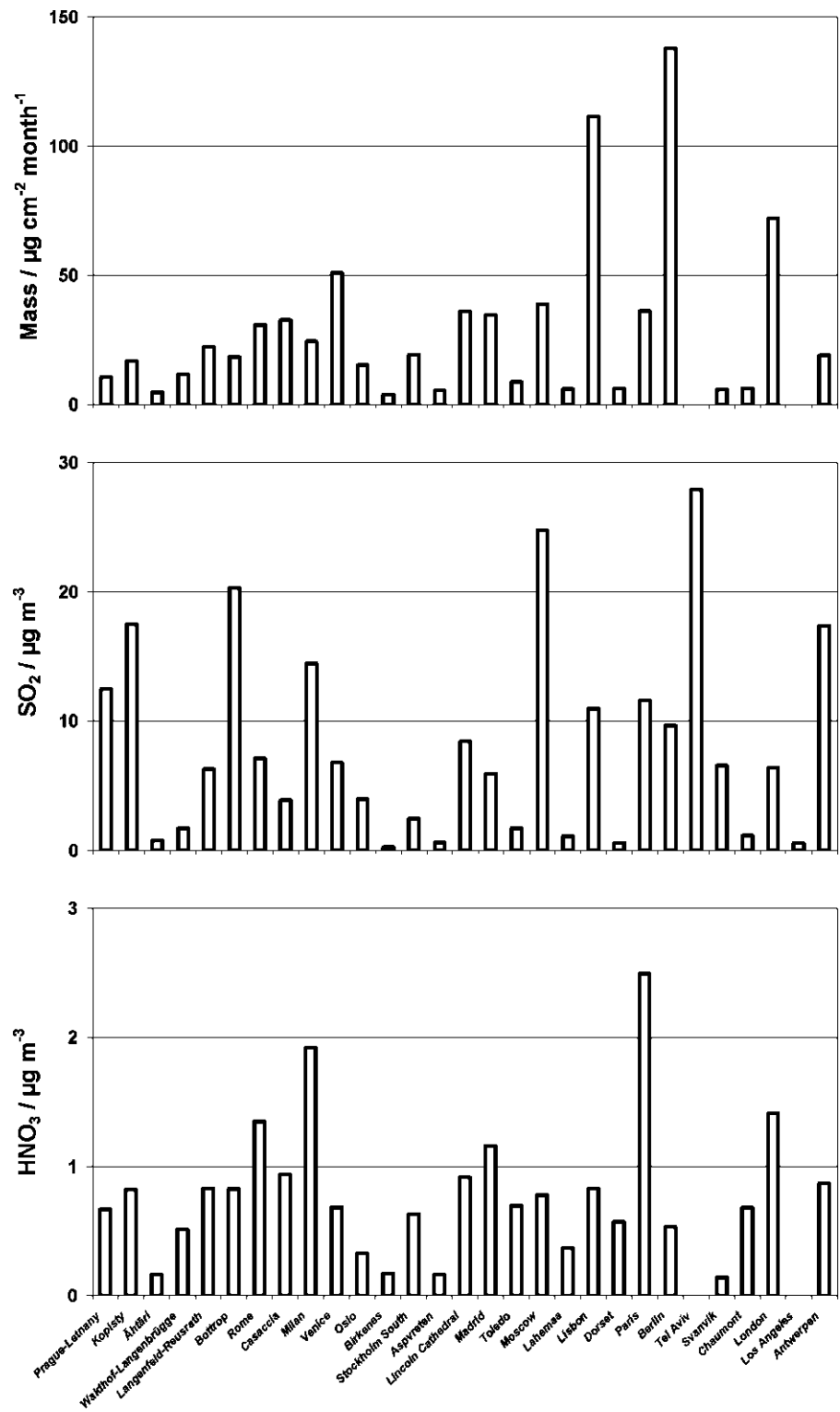


Fig. 3 Corrosion attack of carbon steel, zinc and limestone exposed in the multi-pollutant exposure (1997–2001) for 1 (*left bars*), 2 (*middle bars*) and 4 (*right bars*) years of exposure

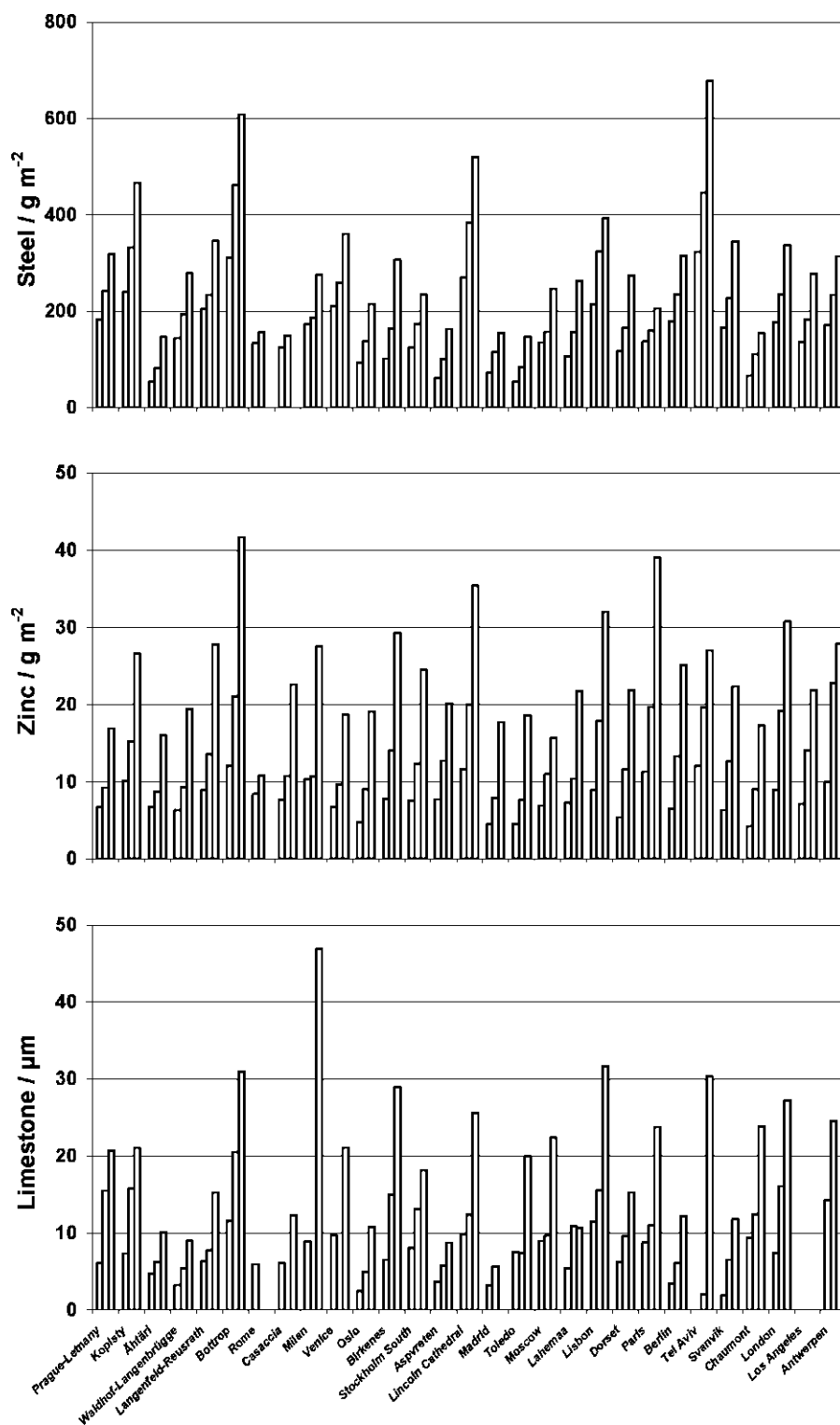


Table 2 Parameters used in the statistical evaluation

Parameter description	Abbreviation	Unit
Time	t	years
Temperature	T	°C
Relative humidity	Rh	%
Amount of precipitation	Rain	mm year ⁻¹
pH of precipitation	pH	decades (dimensionless)
Acidity of precipitation ^a	[H ⁺]	mg l ⁻¹
SO ₂ concentration	[SO ₂]	µg m ⁻³
NO ₂ concentration	[NO ₂]	µg m ⁻³
O ₃ concentration	[O ₃]	µg m ⁻³
HNO ₃ concentration	[HNO ₃]	µg m ⁻³
PM concentration (<10 µm)	PM ₁₀	µg m ⁻³
Mass loss	ML	g m ⁻²
Surface recession	R	µm

^a Calculated directly from pH

where $f(T)$ is as stated above $0.15(T-10)$ when $T < 10^\circ\text{C}$; otherwise $-0.054(T-10)$ and the remaining parameters are given in Table 2.

3.2.2 Zinc

The dose-response function for zinc from the 8-year ICP Materials exposure programme is

$$\text{ML}_{8\text{-year}} = 1.4[\text{SO}_2]^{0.22} e^{0.018\text{Rh}} e^{f(T)} t^{0.85} + 0.029\text{Rain}[\text{H}^+]t$$

where $f(T) = 0.062(T-10)$ when $T < 10^\circ\text{C}$, otherwise $-0.021(T-10)$. Since again the multi-pollutant data set did not disagree with this temperature function it was used in the resulting multi-assess function

$$\text{ML} = 1.82 + t(1.71 + 0.471[\text{SO}_2]^{0.22} e^{0.018\text{Rh}} e^{f(T)} + 0.041\text{Rain}[\text{H}^+] + 1.37[\text{HNO}_3])$$

Table 3 Environmental parameters used in the dose-response functions

Material	T	Rh	Rain	pH	SO ₂	O ₃	HNO ₃	PM ₁₀
carbon steel	X	X	X	X	X			X
zinc	X	X	X	X	X		X	
copper	X	X	X	X	X	X		
bronze	X	X	X	X	X			X
limestone		X	X	X	X		X	X

The main difference between the previous 8-year function and the new multi-pollutant function is the inclusion of HNO₃. This is also a difference between zinc and carbon steel where HNO₃ is not included. Comparing Figs. 2 and 3 this is also manifested when comparing the corrosion attack at the sites Milan and Paris, which both have high HNO₃ levels and the corrosion attack of carbon steel is relatively low while the corrosion attack of zinc and also limestone, which is also affected by HNO₃ (see below), are higher.

3.2.3 Copper

The dose-response function from the 8-year ICP Materials exposure programme is

$$\text{ML}_{8\text{-year}} = 0.0027[\text{SO}_2]^{0.32} [\text{O}_3]^{0.79} \text{Rh} e^{f(T)} t^{0.78} + 0.050\text{Rain}[\text{H}^+]t^{0.89}$$

where $f(T) = 0.083(T-10)$ when $T < 10^\circ\text{C}$, otherwise $-0.032(T-10)$. The multi-pollutant data set did not disagree with this temperature function and the resulting multi-assess function is

$$\text{ML} = 3.12 + t(1.09 + 0.00201[\text{SO}_2]^{0.4} [\text{O}_3]\text{Rh}_{60} e^{f(T)} + 0.0878\text{Rain}[\text{H}^+])$$

The function for copper is very similar to the previously developed function, which also included ozone.

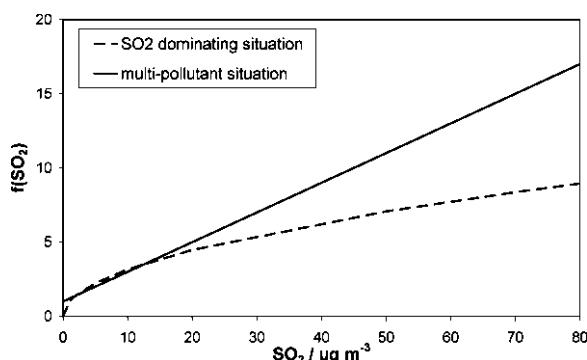


Fig. 4 Illustration of the difference between the SO_2 dependence in dose-response functions for the SO_2 dominating situation and for the multi-pollutant situation

3.2.4 Bronze

The dose-response function from the 8-year ICP Materials exposure programme is

$$\begin{aligned} \text{ML}_{8\text{-year}} = & 0.026[\text{SO}_2]^{0.44} \text{Rhe}^{f(T)} t^{0.86} \\ & + 0.029 \text{Rain}[\text{H}^+] t^{0.76} \\ & + 0.00043 \text{Rain}[\text{Cl}] t^{0.76} \end{aligned}$$

where $[\text{Cl}]$ is the chloride concentration in precipitation (g l^{-1}) and $f(T) = 0.060(T - 11)$ when $T < 11^\circ\text{C}$, otherwise $-0.067(T - 11)$. The multi-pollutant data set did not disagree with this temperature function and the resulting multi-assess function is

$$\begin{aligned} \text{ML} = & 1.33 + t(0.00876[\text{SO}_2]e^{f(T)}\text{Rh}_{60} \\ & + 0.0409 \text{Rain}[\text{H}^+] + 0.038 \text{PM}_{10}) \end{aligned}$$

The main difference between the two functions is that the effect of chloride, expressed as wet deposition, has been replaced with particulate deposition, which may partly be a substitute for a chloride effect term.

3.2.5 Portland Limestone

The dose-response function from the 8-year ICP Materials exposure programme is

$$\begin{aligned} R_{8\text{-year}} = & 2.7[\text{SO}_2]^{0.48} e^{-0.018T} t^{0.96} \\ & + 0.019 \text{Rain}[\text{H}^+] t^{0.96} \end{aligned}$$

The multi-pollutant data set *did* disagree with this temperature function and no effect of temperature

could be estimated. Instead a relative humidity term proved effective for both SO_2 and HNO_3 .

$$\begin{aligned} R = & 3.1 + t(0.85 + 0.0059 \text{Rh}_{60}[\text{SO}_2] \\ & + 0.078 \text{Rh}_{60}[\text{HNO}_3] + 0.054 \text{Rain}[\text{H}^+] \\ & + 0.0258 \text{PM}_{10}) \end{aligned}$$

The new functions should be used in multi-pollutant situations, while the previous ICP Materials functions (Tidblad et al., 2001) are preferable for areas where SO_2 is the dominating pollutant. This is illustrated in Fig. 4. In the interval with moderate SO_2 concentrations ($0\text{--}20 \mu\text{g m}^{-3}$) the difference between the two functions is not significant. The main difference between the two functions is at higher SO_2 concentrations ($60\text{--}80 \mu\text{g m}^{-3}$) where the linear function wrongly predicts higher values.

4 Conclusions

Dose-response functions suitable for mapping and calculations of cost of corrosion damage have been developed for the new multi-pollutant situation for carbon steel, zinc, copper, bronze and limestone exposed in unsheltered position. Both pH and SO_2 are included in all of the functions and these parameters were also present in the previous dose-response functions developed for SO_2 dominating situations. The new functions should be used in multi-pollutant situations, while the previous ICP Materials functions are preferable for areas where SO_2 is the dominating pollutant. Besides SO_2 and acid rain, the effects of HNO_3 and particulate matter have been included in dose-response functions for metallic materials for the first time. NO_2 is not included in any of the functions directly but is closely related to HNO_3 , which is included for zinc and limestone. The effect of particular matter is included for carbon steel, bronze and limestone.

Acknowledgement The ICP Materials exposure programme is the result of co-operation between several signatories to the UN ECE Convention on Long-range Transboundary air pollution, listed on the ICP Materials home page (<http://www.corr-institute.se/ICP-Materials/>). The European Commission is gratefully acknowledged for support to the MULTI-ASSESS project.

References

- Baedecker, P. A. (1990). *NAPAP Report 19: Effects of acidic disposition of materials*. Washington, DC.
- Ferm, M., De Santis, F., & Varotsos, C. (2005). Nitric acid measurements in connection with corrosion studies. *Atmospheric Environment*, 39, 6664–6672.
- Ferm, M., Watt, J., O'Hanlon, S., De Santis, F., & Varotsos, C. (2006). Deposition measurement of particulate matter in connection with corrosion studies. *Analytical and Bio-analytical Chemistry*, in press.
- Haagenrud, S. E., & Henriksen, J. F. (1996). Survey of dose-response (DR) functions for corrosion damage on materials. In V. Kucera, D. Pearce, & Y.-W. Brodin (Eds.), *Proceedings of the UN ECE workshop on economic evaluation of air pollution abatement and damage to buildings including cultural heritage*. Stockholm, Sweden: Swedish Environmental Protection Agency. Report 4761, ISBN 91-620-4761-2.
- ICP Materials. (2003a). *Report No 41. Final environmental data report for the multi-pollutant programme: November 1997–October 2001*. Kjeller, Norway: Norwegian Institute for Air Research.
- ICP Materials. (2003b). *Report No 42. Results from the multi-pollutant programme: Corrosion attack on carbon steel after 1, 2 and 4 years of exposure (1997–2001)*. Prague, Czech Republic: SVUOM Ltd.
- ICP Materials. (2003c). *Report No 43. Results from the multi-pollutant programme: Corrosion attack on zinc after 1, 2 and 4 years of exposure (1997–2001)*. Dübendorf, Switzerland: Swiss Federal Laboratories for Materials Testing and Research (EMPA).
- ICP Materials. (2003d). *Report No 44. Results from the multi-pollutant programme: Corrosion attack on copper and bronze after 1, 2 and 4 years of exposure (1997–2001)*. München, Germany: Bavarian State Department of Historical Monuments.
- ICP Materials. (2003e). *Report No 45. Results from the multi-pollutant programme: Corrosion attack on limestone after 1, 2 and 4 years of exposure (1997–2001)*. Garston, Watford, United Kingdom: Building Research Establishment Ltd. (BRE).
- ICP Materials. (2003f). *Report No 46. Results from the multi-pollutant programme: Corrosion attack on painted steel after 1, 2 and 4 years of exposure (1997–2001)*. Kjeller, Norway: Norwegian Institute for Air Research.
- ICP Materials. (2003g). *Report No 48. Results from the multi-pollutant programme: Evaluation of the decay to glass samples after 3 and 4 years exposure (1997–2001)*. Vienna, Austria: Institute of chemistry, Academy of fine arts.
- ICP Materials. (2004). *Report No 49. Results from the multi-pollutant programme: Evaluation of the decay to glass samples after 3, 4, 5 and 6 years of exposure. Part B: Results of the unsheltered exposure*. Vienna, Austria: Institute of chemistry, Academy of fine arts.
- Kucera, V., Tidblad, J., Samie, F., Schreiner, M., Melcher, M., Kreislova, K., et al. (2005). MULTI-ASSESS publishable final report. <http://www.corr-institute.se/MULTI-ASSESS/>.
- Tidblad, J., Kucera, V., Mikhailov, A. A., Henriksen, J., Kreislova, K., Yates, T., et al. (2001). UN/ECE ICP Materials. Dose-response functions on dry and wet deposition effects after 8 years of exposure. *Water, Air, and Soil Pollution*, 130, 1457–1462.

Long-term Trends in Surface Water Quality of Five Lakes in Japan

T. Yamada • T. Inoue • H. Fukuhara •
O. Nakahara • T. Izuta • R. Suda •
M. Takahashi • H. Sase • A. Takahashi •
H. Kobayashi • T. Ohizumi • T. Hakamata

Received: 16 June 2005 / Accepted: 23 June 2006 / Published online: 12 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Since 1983, the Ministry of the Environment of Japan has conducted nation-wide acid deposition surveys. To investigate the effects of acid deposition on surface water, we used the nonparametric Mann–Kendall test to find temporal trends in pH, alkalinity, and electrical conductivity (EC) in more than 10 years of data collected from five lakes and their catchments (Lake Kuttara: northernmost; Lake Kamakita: near Tokyo; Lake Ijira: central; Lake Banryu: western; and Lake Unagiike: southernmost). The pH of Lake Ijira water has declined slightly since the mid-1990s, corresponding with the downward

trends seen in the pH and alkalinity of the river water flowing into the lake. There were significant upward trends in the EC of both the lake and stream water; the same trends were also found for NO_3^- concentrations. These trends show evidence of acidification due to atmospheric deposition, and this is the first such finding in Japan based on significant long-term trends. Lake Ijira is located about 40 km north of the Chukyo industrial area near Nagoya. The annual depositions of H^+ , nss-SO_4^{2-} , and NO_3^- in Lake Ijira were among the highest of all deposition monitoring sites, suggesting that this is the main cause of the

T. Yamada (✉)
Water Supply Engineering,
National Institute of Public Health,
Wako 351-0197, Japan
e-mail: t-yamada@niph.go.jp

T. Inoue
Department of Architecture and Civil Engineering,
Toyohashi University of Technology,
Toyohashi 441-8580, Japan

H. Fukuhara
Niigata University,
Niigata, Japan

O. Nakahara
Hokkaido University,
Sapporo, Japan

T. Izuta
Tokyo University of Agriculture and Technology,
Fuchu, Tokyo, Japan

R. Suda
Fukuoka Institute of Health
and Environmental Sciences,
Dazaifu, Japan

M. Takahashi
Forestry and Forest Products
Research Institute,
Tsukuba, Japan

H. Sase • A. Takahashi • T. Ohizumi
Acid Deposition
and Oxidant Research Center,
Niigata, Japan

H. Kobayashi
HORIBA, Ltd.,
Kyoto, Japan

T. Hakamata
Hamamatsu Photonics, K.K.,
Tsukuba, Japan

significant acidification observed in Lake Ijira. No significant trends suggesting acidification were observed in any of the other lake catchments in spite of the significant upward trends in EC. Upward trends in pH and alkalinity at Lake Banryu and upward trends in alkalinity at Lake Kamakita were detected, but no change in pH or alkalinity at Lake Kuttara and Lake Unagiike was observed.

Keywords acidification · catchment · long-term trend · surface water · water quality

1 Introduction

In Japan, the Ministry of the Environment has been conducting nation-wide acid deposition surveys since 1983 to clarify the current conditions and the impact of acid deposition. This program, named the Japanese Acid Deposition Survey (JADS), has conducted integrated surveys at five lakes and their catchments examined in this paper for almost 20 years, carrying out long-term monitoring of wet deposition, dry deposition, soil, vegetation, and the lakes' aquatic environments. Some of these surveys will continue as part of the acid deposition monitoring network in East Asia (EANET). International cooperative programs on the assessment and monitoring of acid deposition and on control of emissions, and the accompanying international regulations and agreements, have been in place in Europe since the Convention on Long-Range Transboundary Air Pollution (CLRTAP) was signed in 1979 (Kvaeven, Ulstein, Skjelkvale, Raddum, & Hovind, 2001). Long-term trend analyses of surface water have shown declines in the rate of acid deposition and the widespread recovery of surface water acidification in European countries (Skjelkvale, Stoddard, & Andersen, 2001; Stoddard et al., 1999). Although global sulfur emissions peaked in 1987 and declined rapidly thereafter, Asia was the largest sulfur emitter in the world in 2000 (Stern, 2005). Possible adverse impacts caused by acid deposition are of concern in some parts of China (Ye, Hao, Duan, & Zhou, 2002). In Japan, no long-term effects of acid deposition have so far been seen on surface water, because of the high acid-neutralizing capacity of the surrounding terrain (Ohte et al., 2001); although temporal decreases in pH in the surface waters were

observed during rainfall (Komai, Umemoto, & Inoue, 2001). In this study, more than 10 years of data collected by JADS from five lake catchments were tested for temporal trends in pH, alkalinity, and electrical conductivity (EC) by the nonparametric seasonal Mann–Kendall test to clarify significant effects of acid deposition on surface waters in Japan.

2 Materials and Methods

The study sites in Japan were Lake Kuttara (northernmost), Lake Kamakita (near Tokyo), Lake Ijira (central), Lake Banryu (western), and Lake Unagiike (southernmost) (Fig. 1). These lakes were selected by JADS as representative of the major types of lakes in Japan. Lake Ijira and Lake Kamakita were selected as monitoring sites to clarify the impact of two major industrial areas in Japan, the Chukyo industrial area located near Nagoya City in central Japan and the Keihin industrial area in the Tokyo Bay area, respectively. Lake Kuttara and Lake Unagiike represent Japan's northernmost and southernmost caldera lakes, respectively. Lake Banryu is located in a region that would be affected by atmospheric deposition from continental Eurasia. Lake Ijira and Lake Banryu are EANET monitoring sites. General information on these five lakes, including the bedrock geology, type

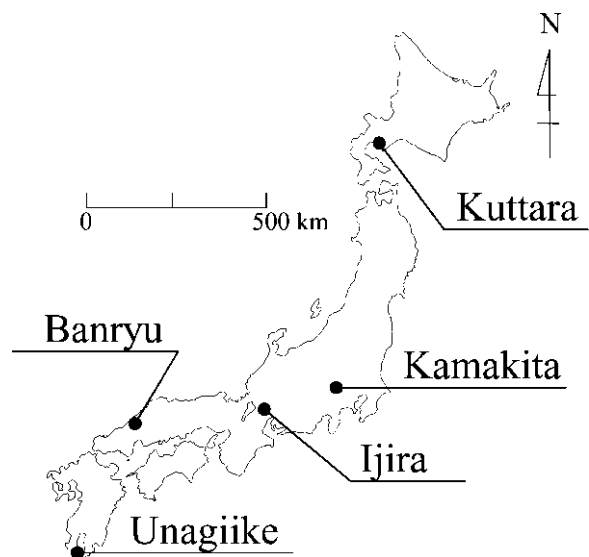


Fig. 1 Map of Japan showing locations of the studied sites

Table 1 General information on the geology, surface soil, and vegetation in the catchments of the studied lakes

			Lake Kuttara	Lake Kamakita	Lake Ijira	Lake Banryu	Lake Unagiike
Lake	Type		Caldera	Dammed lake	Dammed lake	Dammed lake	Caldera
	Area of lake	km ²	4.7	0.035	0.1	0.13	1.15
	Average depth	m	105.1	6.83	5.4	5	34.8
	Catchment area	km ²	3.41	2.21	5.3	0.73	2.45
	Bedrock		Volcanic rock, non-alkaline mafic rock; formed in the late Pleistocene	Sedimentary rock, chert including schalstein and limestone; formed in the Paleozoic	Chert and mudstone; formed in the Mid Jurassic to Early Cretaceous	Sedimentary rock	Volcanic rock, non-alkaline mafic rock; formed in the Quaternary
	Surface soil		Brown forest soil, Volcanic ash soil	Brown forest soil	Brown forest soil	Brown forest soil	Andosol, Red-yellow soil
	Vegetation		Japanese oak, Gold birch	Japanese cedar, Japanese cypress	Japanese cypress, Japanese cedar, Japanese red pine	Japanese red pine, Japanese black pine	Japanese cypress, Japanese cedar
Lake	pH		7.51	8.24	7.20	7.09	8.15
water	EC	mS/m	6.40	13.65	4.38	9.91	11.90
quality	Alk.	μeq/L	305	857	151	136	602
	SO ₄ ²⁻	mg/L	6.66	7.85	5.81	4.80	6.95
	NO ₃ ⁻	mg/L	0.31	7.20	1.31	0.01	<0.002
	Cl ⁻	mg/L	4.15	4.35	2.53	21.2	12.95
	NH ₄ ⁺	mg/L	<0.06	<0.06	0.03	0.015	0.002
	Na ⁺	mg/L	5.23	3.30	2.52	13.37	9.20
	K ⁺	mg/L	0.48	0.73	0.59	1.64	2.20
	Ca ²⁺	mg/L	3.59	15.00	4.86	1.56	9.50
	Mg ²⁺	mg/L	1.98	4.60	1.50	1.84	3.20
	^a COD	mg/L	0.9	3.5	1.4	4.9	2.6
	^b Chl-a	μg/L	0.5	21.4	5.1	4.5	2.9

Median values of water chemistry from 1995 to 1997 in surface water from the center of the lakes are also shown.

^aChemical Oxygen Demand

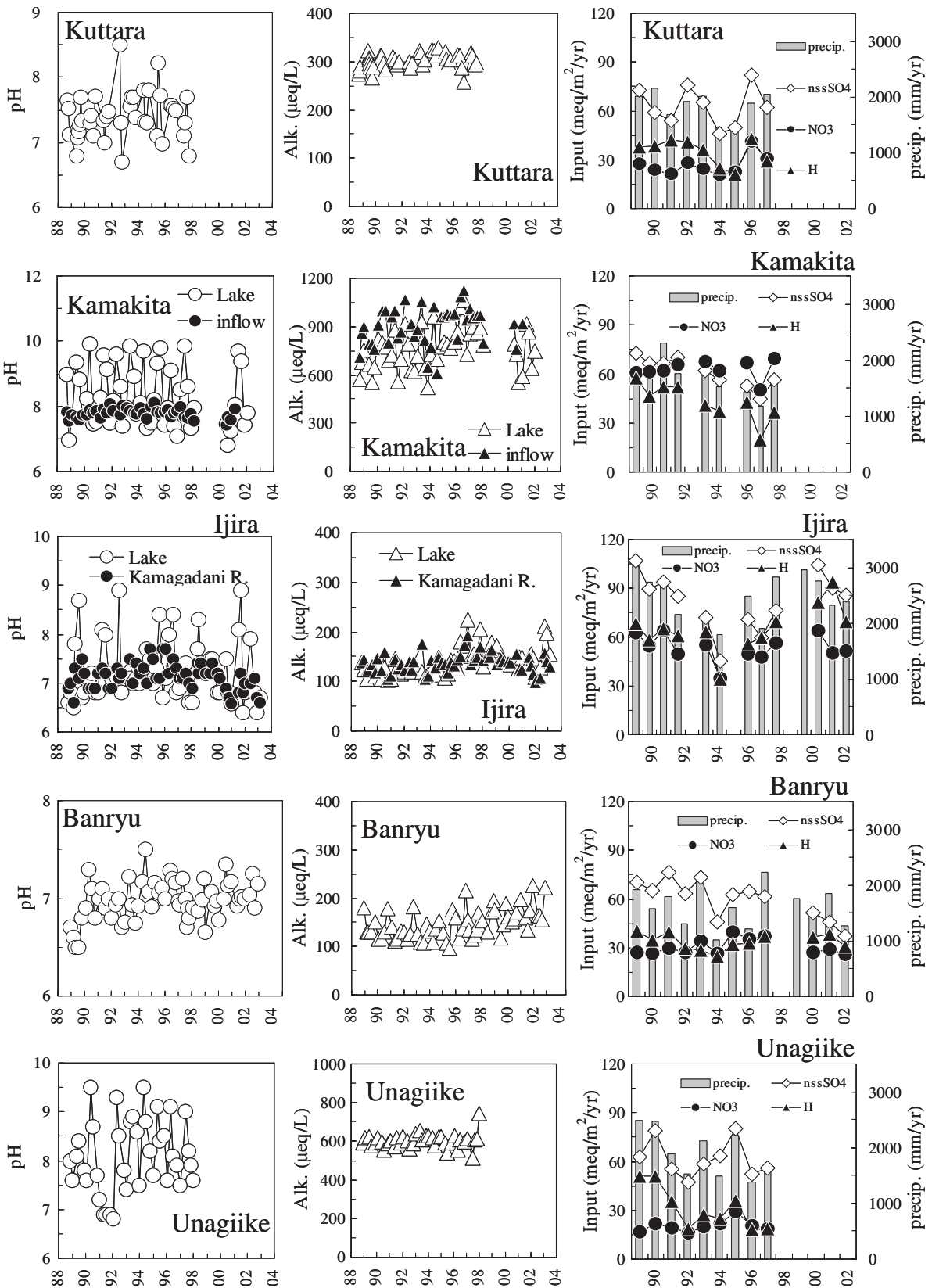
^bChlorophyll a

of dominant surface soil, vegetation, and the average concentrations of major ions in the surface water at the center of the lakes is summarized in Table 1. Surveys of lake water were conducted four times a year from September 1988 to October 1997 at Lake Kuttara and from October 1998 to January 1998 at Lake Unagiike. Surveys of water from Lake Kamakita and river water flowing into the west end of the lake were conducted from September 1988 to February 2002, with the exception of the period from March 1998 to June 2000 because of dredging in the lake. Surveys of lake water and river water were conducted four times a year from September 1998 to March 2003 at Lake

Ijira, and surveys of water from Lake Banryu were conducted from November 1988 to December 2002.

Wet precipitation was collected monthly with a bulk precipitation collector from October 1988 to March 1998 at the five sites. Wet precipitation has also been collected weekly by a wet-only precipitation collector since June 1999 at Lake Ijira and Lake Banryu.

For detecting long-term trends in pH, alkalinity, and EC in the water of the studied sites, the seasonal Mann–Kendall test was used. The seasonal Mann–Kendall test is a non-parametric test for detection of monotonic trends that accommodates non-normal data distribution (Helsel & Hirsch, 1992).



◀ **Fig. 2** Temporal variations in pH (*left*) and alkalinity (Alk.) (*center*) in surface lake water at the center of each lake and the river water flowing into Lake Kamakita and Lake Ijira. Annual rates of acid deposition (H^+ (H), nss- (nssSO₄), and (NO₃)) and annual amount of precipitation (precip.) at each lake site are shown on the *right*

3 Results

The variations in pH and alkalinity of the surface water at the center of each of the five lakes and of the river water flowing into Lake Kamakita and Lake Ijira are shown in Fig. 2. Table 2 shows the results of the seasonal Mann–Kendall tests for these variations in

pH, alkalinity, and EC at the sites over the whole monitoring period.

In Lake Kuttara, the pH of the lake water was between 7 and 8, and there was no significant increasing or decreasing trend over the 10 years, although there was a significant increase in the trend of EC. No change in alkalinity (about 300 $\mu\text{eq/L}$) was observed in Lake Kuttara; therefore, no evidence of impact by acid deposition was seen.

Lake Kamakita had a large seasonal change in pH, but no significant increase or decrease in the trend of pH was observed over the monitoring period. Alkalinity in both lake water and river water flowing into

Table 2 Results of trend analyses on the pH, alkalinity, and EC in lake and river water of the five study sites

Site	Peroid	Sampling point	pH trend		Alkalinity trend		EC trend			
			<i>N</i>	Z-score	<i>N</i>	Z-score	<i>N</i>	Z-score		
Kuttara	1988	Lake	center (surface)	28	0.51	28	1.08	28	1.58	
	~		center (50 m)	28	0.91	28	0.06	28	2.26*	
	1997		east (surface)	28	0.63	28	0.49	28	0.46	
			west (surface)	28	0.90	28	1.24	28	1.35	
Kamakita	1988	Lake	center (surface)	39	−0.32	39	1.16	39	−0.05	
	~		west (surface)	39	−1.07	39	3.84**	39	3.30**	
	1997	Inflow	river to the lake	39	0.05	39	2.69**	39	2.41*	
Ijira	1988	Lake	center (surface)	38	−0.05	38	2.46*	38	4.57**	
	~		center (8 m)	38	−0.79	38	1.87	38	3.99**	
	1997		north (surface)	38	0.74	38	2.22*	38	4.19**	
			east (surface)	38	0.44	38	2.54*	38	4.43**	
		Inflow	Kamagadani River	38	1.82	38	1.26	38	3.41**	
			Kohbora River	29	−0.07	29	1.97*	29	1.42	
	1988	Lake	center (surface)	57	−1.05	57	4.04**	57	5.61**	
	~		Inflow	Kamagadani River	57	−0.49	57	0.56	57	2.76**
	2003		Kohbora River	40	−1.73	40	1.47	40	2.89**	
	1995	Lake	center (surface)	31	−1.18	31	0.00	31	1.16	
	~		Inflow	Kamagadani River	31	−2.89**	31	−1.81	31	−1.16
	Banryu	2003		Kohbora River	22	−2.03*	22	−0.49	22	1.47
1988		Lake	center (surface)	38	3.14**	38	0.00	38	3.78**	
			~	center (bottom)	37	1.46	37	0.70	37	4.47**
		1997	west (surface)	38	2.95**	38	−0.53	38	2.94**	
			east (surface)	38	4.41**	38	0.39	38	3.76**	
			eastmost (surface)	38	4.09**	38	1.15	38	4.43**	
1988		Lake	center (surface)	56	2.02*	56	3.12**	56	3.03**	
~			center (bottom)	54	2.03*	54	3.32**	54	5.14**	
2002			east (surface)	56	3.31**	56	4.15**	56	2.44*	
Unagiike		1988	Lake	center (surface)	37	0.61	37	0.45	37	5.34**
		~		center (50 m)	35	1.64	34	−1.16	35	4.64**
		1997		northwest (surface)	37	1.61	37	0.60	37	5.13**

Positive Z-scores by the seasonal Mann–Kendall tests indicate increasing trends while negative Z-scores indicate decreasing trends. Z-scores lower than −1.96 or higher than 1.96 indicate significant decreases or increases ($P < 0.05$) shown in bold in the table. Results of analyses for Lake Ijira water from 1995 to 2003 are also shown.

* $p < 0.05$, ** $p < 0.01$. Significant trends ($p < 0.05$) are shown in bold.

Lake Kamakita was more than 500 $\mu\text{eq/L}$, which means that the water in Lake Kamakita had a high acid-buffering capacity. Trend analysis for Lake Kamakita water from 1988 to 1997 (Table 2) showed significant increasing trends in the alkalinity and EC. The alkalinity and EC in the river water flowing into the west end of Lake Kamakita also had significant upward trends, corresponding to significant increases in Ca^{2+} and NO_3^- ($P < 0.05$) (T. Yamada, unpublished data). There was no evidence of acidification in Lake Kamakita before 1997, whereas after 2000 the pH and alkalinity in some samples of lake and river water were lower than those before 1997 (Fig. 2).

The alkalinity of the water in Lake Ijira and the rivers flowing into it was about 150 $\mu\text{eq/L}$, which was relatively low compared to the other sites. The EC in the lake and river water and the alkalinity in lake surface water showed significant increasing trends, whereas no significant trend was detected in pH in lake water and either pH or alkalinity in river water for the 10 years of data since 1988. The pH of the water in Lake Ijira has declined slightly since the mid-1990s, corresponding to the downward trends in the pH of the river water flowing into the lake (Fig. 2). The alkalinity of the river water has also shown a decreasing trend since the mid-1990s. After 1995,

there were significant decreasing trends in pH in the rivers flowing into Lake Ijira and a slightly decreasing trend in alkalinity in one of the rivers ($P < 0.1$) (Table 2).

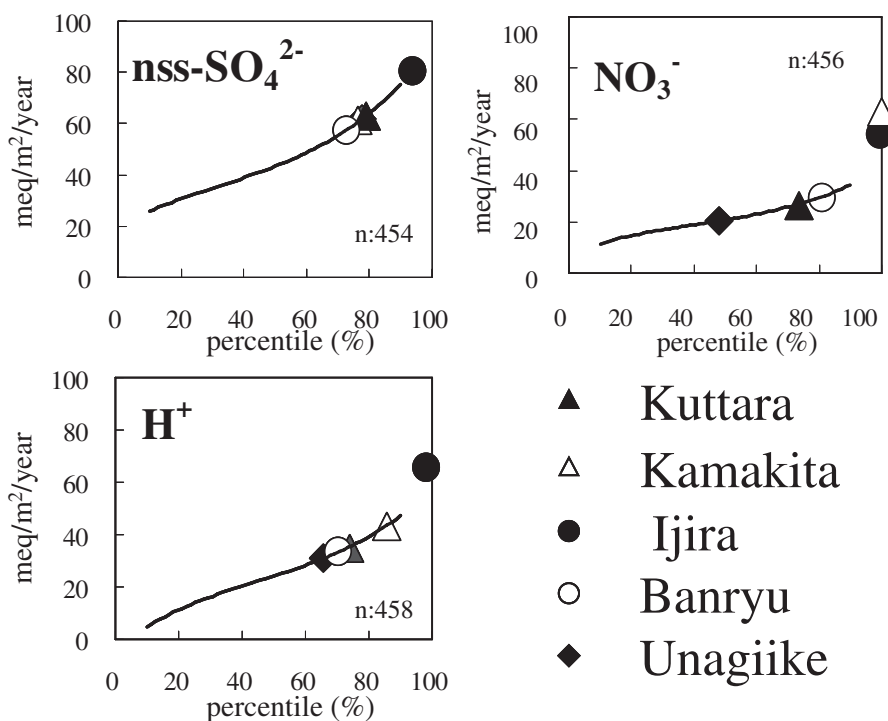
The water of Lake Banryu was affected by sea salt, and the concentrations of Na^+ and Cl^- in the lake water were higher than those in the other lakes (Table 1). The pH and alkalinity of surface water in the center of the lake were relatively low, ranging from 6.5 to 7.6 and from 100 to 250 $\mu\text{eq/L}$, respectively. Lake Banryu had increasing trends in pH, alkalinity, and EC over the study period. These upward trends in pH and alkalinity indicate the alkalization of Lake Banryu water.

In Lake Unagiike, there was some seasonal fluctuation in pH, but the long-term trend analysis detected no change. Alkalinity in the lake was high, at about 600 $\mu\text{eq/L}$, with little seasonal fluctuation. Lake Unagiike also had increasing trends in EC over the study period.

4 Discussion

The rates of acid deposition (as H^+ , nss-SO_4^{2-} , and NO_3^-) at the five monitoring sites in this paper were

Fig. 3 Ogive of the rate of acid deposition in the five study sites and the other JADS monitoring sites in Japan (Committee for Acid Deposition Measures, 2004)



among the highest of all sites included in the JADS surveys on acid deposition (Committee for Acid Deposition Measures, 2004). Nevertheless, most of the sites showed no significant trends revealing acidification of the water, such as pH decline (Fig. 3). Lake Kuttara and Lake Unagiike are both caldera lakes with no inflowing rivers, and their catchments are covered with volcanic rocks with high acid-buffering capacity, which is the reason there is no trend toward acidification. That there was no evidence for acidification in Lake Kamakita water over the monitoring period was also due to the geology of the Lake Kamakita catchment, which includes bedrock with high acid-buffering capacity, such as limestone (Table 1). The rate of NO_3^- deposition in Lake Kamakita, located near the Keihin industrial area, was among the highest in Japan (Fig. 3) suggesting that the significant trend of increasing NO_3^- in Lake Kamakita is due to acid deposition. The concentrations of NO_3^- in precipitation have increased in the Tokyo metropolitan area since 1990 (Okuda et al., 2004) and continuous monitoring of Lake Kamakita is needed in the future.

Acidification in the inflowing river water and in the lake water was detected by the long-term monitoring only in the Lake Ijira catchment. The Lake Ijira catchment is unpopulated and there are no natural acidification factors, such as volcanoes, or artificial sources of pollution in the catchment. The alkalinity of both the river water and the water in Lake Ijira was low among the lakes studied. The bedrock of the Lake Ijira catchment is mainly chert with low acid-buffering capacity and brown forest soils with low acid-buffering capacity are dominant in the catchment. This indicates that the aquatic environment of Lake Ijira is more sensitive to acid deposition than the aquatic environments of the other catchments. The rate of acid deposition in Lake Ijira was among the highest of all the monitoring sites in Japan (Fig. 3). Lake Ijira is located about 40 km north of the Chukyo industrial area near Nagoya, one of the biggest industrial areas in Japan. Air pollution from this industrial area is transported to the mountainous areas that include the Lake Ijira catchment (Kitada, Okamura, Nakanishi, & Mori, 2000). In the Lake Ijira catchment, the change in estimated proton loads due to acid deposition from 1989 to 1997 was consistent with the change in pH in surface water; the estimated proton load due to atmospheric deposition was larger

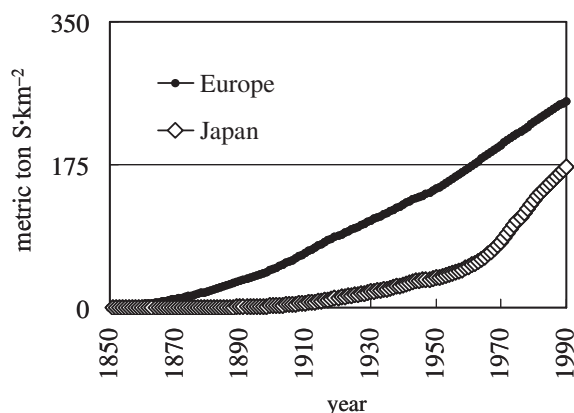


Fig. 4 Estimated accumulated emissions of sulfur in Japan and Europe since 1850 (Lefohn et al., 1999)

than the rate of carbonic acid weathering (O. Nakahara, unpublished data), leading to the conclusion that the significant decline in pH and alkalinity in Lake Ijira is because of acid deposition acidifying inland waters. This is the first time in Japan that the results of long-term monitoring have pointed to acidification of surface water by acid deposition.

Because of the high acid-neutralizing capacity of the geology, acid deposition has so far had no obvious effect on acidification of surface waters in Japan (Ohte et al., 2001). Most of the lakes in this study also showed no long-term trend toward acidification. However, the estimated accumulated emission of sulfur in Japan since 1850 is almost the same now as that in Europe in the 1960s (Fig. 4; Lefohn, J. D. Husar, & R. B. Husar, 1999), suggesting that the impact of acid deposition might soon become obvious in Japan in regions, such as Lake Ijira, where the catchment is relatively sensitive to acidification and where there are high loads of acid deposition.

5 Conclusions

Analysis of the data collected during the long-term monitoring of five representative lakes showed acidification due to acid deposition in the Lake Ijira catchment since the mid-1990s. Changes such as the alkalization of lake water and increases in EC were also detected in the other sites in this study, but we observed no evidence of acidification in sites other than Lake Ijira. The acidification in Lake Ijira was related to the geology of the catchment and the rate of acid deposition loading.

References

- Committee for Acid Deposition Measures. (2004). Comprehensive Report on Acid Deposition Survey (in Japanese), the Ministry of the Environment, Japan, p. 432.
- Helsel, D., & Hirsch, R. (1992). *Statistical methods in water resources: Studies in environmental science* 49 (pp. 323–355). New York: Elsevier.
- Kitada, T., Okamura, K., Nakanishi, H., & Mori, H. (2000). Production and transport of ozone in local flows over central Japan – Comparison of numerical calculation with airborne observation. In *Air pollution modeling and its application XIII* (pp. 95–106). New York: Plenum.
- Komai, Y., Umemoto, S., & Inoue, T. (2001). Influence of acid deposition on inland water chemistry – A case study from Hyogo prefecture, Japan. *Water, Air, and Soil Pollution*, 130, 1535–1540.
- Kvaeven, B., Ulstein, M. J., Skjelkvale, B. L., Raddum, G. G., & Hovind, H. (2001). ICP waters – An international programme for surface water monitoring. *Water, Air, and Soil Pollution*, 130, 775–780.
- Lefohn, A. S., Husar, J. D., & Husar, R. B. (1999). Estimating historical anthropogenic global sulfur emission patterns for the period 1850–1990. *Atmospheric Environment*, 33(21), 3435–3444.
- Ohte, N., Tokuchi, N., Shibata, H., Tsujimura, M., Tanaka, T., & Mitchell, M. J. (2001). Hydrobiogeochemistry of forest ecosystems in Japan: Major themes and research issues. *Hydrological Processes*, 15, 1771–1789.
- Okuda, T., Iwase, T., Ueda, H., Suda, Y., Tanaka, S., Dokiya, Y., et al. (2004). Long-term trend of chemical constituents in precipitation in Tokyo metropolitan area, Japan, from 1990 to 2002. *Science of the Total Environment*, 339, 127–141.
- Skjelkvale, B. L., Stoddard, J. L., & Andersen, T. (2001). Trends in surface water acidification in Europe and North America (1989–1998). *Water, Air, and Soil Pollution*, 130, 787–792.
- Stern, D. I. (2005). Global sulfur emissions from 1850 to 2000. *Chemosphere*, 58, 163–175.
- Stoddard, J. L., Jeffries, D. S., Lukewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., et al. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature*, 401, 575–578.
- Ye, X., Hao, J., Duan, L., & Zhou, Z. (2002). Acidification sensitivity and critical loads of acid deposition for surface water in China. *Science of the Total Environment*, 289, 189–203.

The Fernow Watershed Acidification Study: Ecosystem Acidification, Nitrogen Saturation and Base Cation Leaching

Mary Beth Adams · James N. Kochenderfer ·
Pamela J. Edwards

Received: 13 June 2005 / Accepted: 3 April 2006 / Published online: 17 January 2007
© Springer Science + Business Media B.V. 2007

Abstract In 1989, a watershed acidification experiment was begun on the Fernow Experimental Forest in West Virginia, USA. Ammonium sulfate fertilizer ($35.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $40.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was applied to a forested watershed (WS3) that supported a 20-year-old stand of eastern deciduous hardwoods. Additions of N and S are approximately twice the ambient deposition of nitrogen and sulfur in the adjacent mature forested watershed (WS4), that serves as the reference watershed for this study. Acidification of stream water and soil solution was documented, although the response was delayed, and acidification processes appeared to be driven by nitrate rather than sulfate. As a result of the acidification treatment, nitrate solution concentrations increased below all soil layers, whereas sulfate was retained by all soil layers after only a few years of the fertilization treatments, perhaps due to adsorption induced from decreasing sulfate deposition. Based on soil solution monitoring, depletion of calcium and magnesium was observed, first from the upper soil horizons and later from the lower soil horizons. Increased base cation concentrations in stream water also were documented and linked closely with high solution levels of nitrate.

Significant changes in soil chemical properties were not detected after 12 years of treatment, however.

Keywords acidic deposition · base cation leaching · forest soils · nitrogen saturation · soil solution chemistry

1 Introduction

In 1989, the Fernow Watershed Acidification Study began when experimental additions of ammonium sulfate first were made to a small forested watershed (WS3). An adjacent forested watershed (WS4) containing an older stand uncut since 1905, serves as a reference watershed for stream water and soil water chemistry. For vegetation comparisons, watershed 7 (WS7) is used because the stands began regrowth at the same time, in the spring of 1970 (Table 1). The original objective was to evaluate impacts of atmospheric deposition on stream water and soil leachate chemistry. Additional opportunistic research has addressed the effects of acidification on soil chemistry, amphibian populations, tree and stand growth, and nutrient cycling, among other topics. In this manuscript, we highlight some of the major biogeochemical findings from the Fernow Watershed Acidification Study, focusing on the processes of acidification, nitrogen (N) saturation, and base cation leaching.

M. B. Adams (✉) · J. N. Kochenderfer · P. J. Edwards
USDA Forest Service,
P.O. Box 404, Parsons, WV 26287, USA
e-mail: mbadams@fs.fed.us

Table 1 Some characteristics of the study watersheds, Fernow Experimental Forest, West Virginia, USA

Characteristic	WS3	WS4	WS7
Area (ha)	34	39	24
Aspect	South	Southeast	East
Stand age (yrs)	34	95	34
Mean stand density (stems ha ⁻¹)	1,883	1,206	1,473
Mean stand biomass (mt ha ⁻¹)	203.4	310.7	157.5
Dominant tree species (% basal area)	Black cherry (51.0)	Sugar maple (1.3)	Sugar maple (4.9)
	Red maple (11.5)	Red maple (8.9)	Sweet birch (20.5)
	American beech (2.5)	American beech (6.5)	Red maple (8.2)
	Sweet birch (5.1)	Northern red oak (29.8)	Yellow-poplar (26.2)
	Sugar maple (11.3)	Sweet birch (3.6)	Black cherry (20.5)

Stand parameters are based on the 1990 inventory for WS4, 2004 for WS3 and WS7.

2 Site Description

The Fernow Experimental Forest (FEF; 39.03°N, 79.67°W) is in north-central West Virginia, in the Allegheny Mountain section of the mixed mesophytic forest, within the central Appalachian Mountains. Prior to settlement, central Appalachian forests were shaped by disturbances such as wind, fire, and agricultural use, creating a diverse mosaic of forest stands. Recently, several insects and diseases, most of them non-native, have severely impacted Appalachian forests, and acidic deposition and other air pollutants represent a chronic disturbance (Adams, 1999).

Diversity is a hallmark of central Appalachian forests, such as the FEF, and the vegetation fits into Core's (1966) mixed central hardwood forests floristic province. Madarish, Rodrigue, and Adams (2002) lists more than 500 species of vascular flora found on the FEF. Common tree species include yellow-poplar (*Liriodendron tulipifera* L.), sugar maple (*Acer saccharum* Marsh.), black cherry (*Prunus serotina* Ehrh.), northern red oak (*Quercus rubra* L.) red maple (*A. rubrum* L.), American beech (*Fagus grandifolia* Ehrh.), and sweet birch (*Betula lenta* L.), although their distribution is highly variable across the watersheds (Table 1).

The growing season on the FEF extends from May through October, and the average length of the frost free season is 145 days. Annual precipitation is about evenly distributed between growing and dormant seasons, averaging 145.8 cm. Precipitation often occurs in the form of snow during the winter but a snowpack usually does not exist for extended periods. Average annual air temperature is 9.2°C

(Pan, Tajchman, & Kochenderfer, 1997), and mean monthly temperatures range from -18°C in January to 20.6°C in July. Potential evapotranspiration on the Fernow was estimated to be 56 cm/year (Patric & Goswami, 1968).

The hydrometeorologic network of the Fernow is described by Adams, Kochenderfer, Wood, Angradi, and Edwards (1994). WS3, WS4, and WS7 are instrumented with 120° V-notch weirs, with FW-1 water level recorders and 7-day strip charts to measure streamflow continuously. Stream water grab samples have been collected from WS3, WS4, and WS7 on a weekly or bi-weekly basis since 1960. In addition to grab sampling, stream water also was sampled during storm runoff events using automatic pumping samplers. Zero-tension pan lysimeters were installed on WS3 and WS4 in 1988 to sample soil water for chemical analyses. Stream and soil water samples were analyzed at the USDA Forest Service Timber and Watershed Laboratory in Parsons, West Virginia, USA, using U.S. Environmental Protection Agency protocols (Edwards & Wood, 1993).

2.1 Watershed Acidification Treatment

Ammonium sulfate fertilizer was applied to WS3 at a rate that approximately doubled bulk deposition inputs of N and S estimated from throughfall concentrations (Helvey & Kunkle, 1986). Applications were made in spring, summer, and autumn (usually in March, July, and November) to reflect seasonal variability in deposition. Spring and autumn application rates were 34 kg fertilizer ha⁻¹ (7.1 kg N ha⁻¹ and 8.1 kg S ha⁻¹), respectively. Summer application

rates were 101 kg fertilizer ha⁻¹ (21.3 kg N ha⁻¹ and 24.4 kg S ha⁻¹). All applications on WS3 during the first 9 years were made by helicopter; beginning in July 1998 all applications to WS3 have been made by low flying fixed-wing aircraft equipped with a global positioning swathing system to ensure accurate coverage.

3 Results and Discussion

Application of ammonium sulfate fertilizer to WS3 during the Fernow Watershed Acidification Study has resulted in significant changes to several watershed parameters. Some of these effects were obvious and were consistent with published models of ecosystem acidification, N saturation and base cation cycling (Aber et al., 1998; Galloway, Norton, & Church, 1983; Norton, Fernandez, Kahl, & Reinhardt, 2003; Stoddard, 1994), while other effects were less so.

3.1 Acidification Processes

Fertilizer additions were effective in acidifying the ecosystem on WS3, based on stream and soil solution chemistry (Figs. 1 and 2). Additions of sulfate via the fertilizer treatment increased leaching of sulfate in stream water over time (Fig. 1). However, the sulfate response was not as rapid nor as substantial as we had hypothesized. Early in the experiment nitrate seemed to be a more important driver of changes in stream water chemistry. Sulfur retention by WS3 ranged from 72 to 91% of that applied (calculated from input–output budgets), and decreased slightly over time, but this decline was observed on most of the monitored watersheds on the FEF, not just WS3 (Adams, DeWalle, & Hom, 2006). Significant declines in ambient sulfate deposition during the course of the experiment (Lynch, Bowersox, & Grimm, 2000) could partially explain these results, as adsorption of sulfate is a partially reversible process and concentration-dependent (Reuss & Johnson, 1986).

Baseflow stream pH on WS3 decreased approximately 0.8 pH units, from around 6.0 to about 5.2, during the study (Fig. 1). Increased acidity on WS3 was statistically significant and resulted in WS3 baseflow moving from being only episodically acidic to chronically acidic based on stream pH and acid

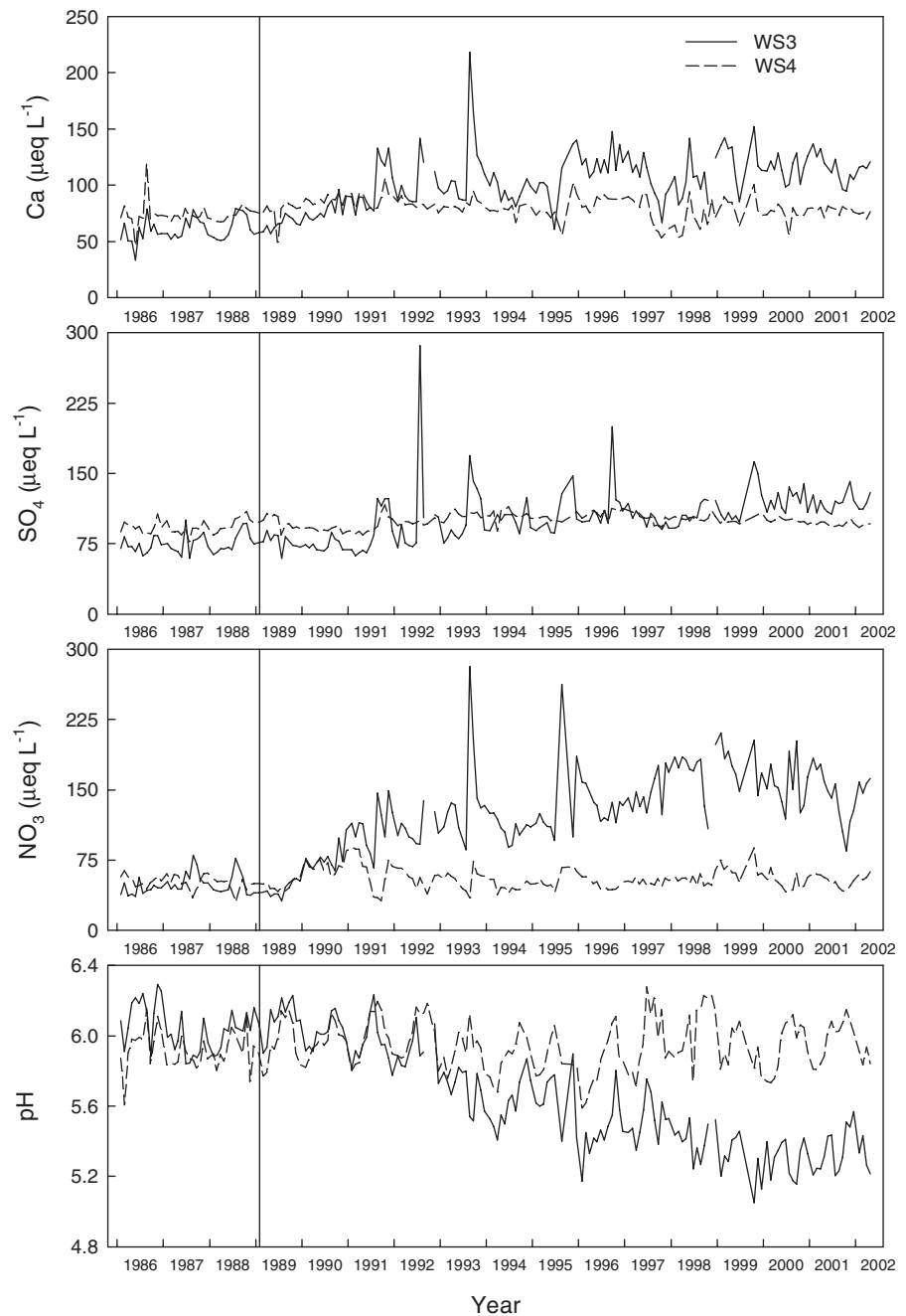
neutralizing capacity (ANC). A similar trend occurred for peakflow (Edwards, Williard, Wood, & Sharpe, 2006). Significant decreases in soil solution pH also indicate acidification (Fig. 2). However, soil chemical parameters were much less responsive to the treatments, and few significant differences in soil chemical parameters were detected between WS3 and WS4 soil chemistry, regardless of horizon sampled (Adams et al., 2006). This lack of treatment effect can be attributed at least partially to high spatial variability in soil chemistry within the watersheds (Adams et al., 2006; Gilliam, Yurish, & Adams, 2001; Peterjohn, Adams, & Gilliam, 1996). Also, soil solution chemistry may not mirror bulk soil chemistry, as the soil water collected in zero tension lysimeters reflects channelized or macropore flow.

3.2 N Saturation

The fertilizer additions also affected N cycling on WS3, and may have induced N saturation (Aber et al., 1998; Peterjohn et al., 1996; Stoddard, 1994). The added N rapidly resulted in increased stream water nitrate concentrations (Fig. 1). Increased fluxes of nitric oxide (NO) gas also were detected (Venterea et al., 2004) in response to the treatment, along with decreased resorption of N prior to leaf senescence (May, Burdette, Gilliam, & Adams, 2005). Significant increases in foliar N concentrations on WS3 relative to WS7 were detected in 1992 for black cherry and red maple, but differences were not significant in 2002 foliage samples (DeWalle et al., 2006). These results provide some support for the idea of N saturation of the forest on WS3.

However, there was a significant positive growth response on WS3 plots dominated by black cherry and yellow poplar (Fig. 3). Biomass and volume growth on the treated WS3 exceeded that observed on WS7 for the 14 year measurement period, suggesting that N was limiting on WS3 for the entire measurement period, which appears to be inconsistent with models of N saturation (Aber et al., 1998; Stoddard, 1994). Other results also raise questions about the N status of these watersheds. For example, the Aber et al. (1998) model predicts that N mineralization will initially increase then decrease, while net nitrification increases. Yet despite additions of almost 500 kg ha⁻¹ of N to WS3 between 1989 and 2003, no significant differences in net N mineralization and nitrification

Fig. 1 Flow-weighted mean monthly stream water concentrations of Ca, SO₄, NO₃ and stream pH for WS3 (solid line) and WS4 (dashed line), Fernow Experimental Forest, West Virginia, USA. Vertical bar represents start of the ammonium sulfate fertilizer additions to WS3

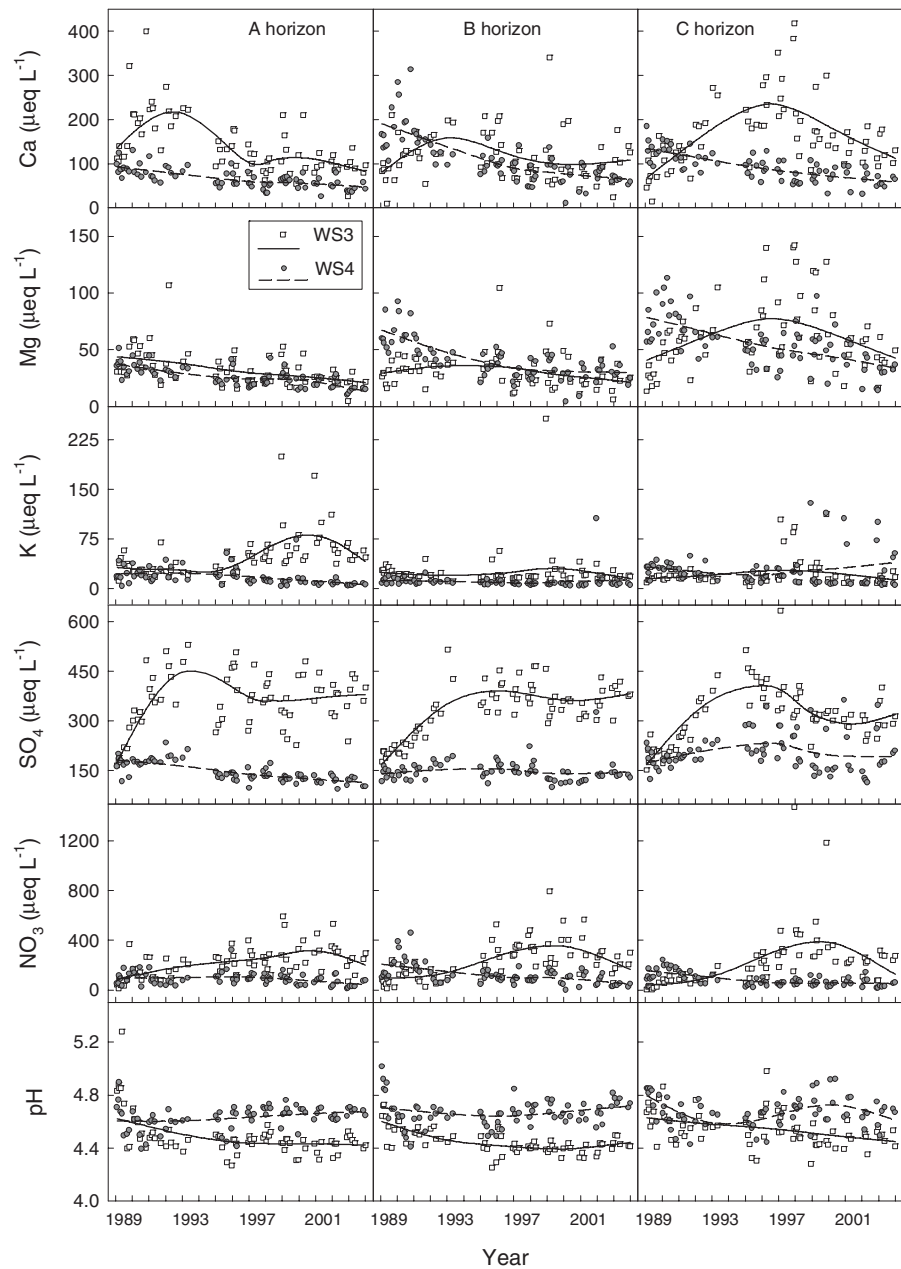


rates could be detected between the watersheds, and rates were consistently high (Gilliam et al., 2001). Also, prior to initiation of the treatment, WS3 retained approximately 55% of N inputs from deposition (calculated from input–output budgets). Retention of the added fertilizer N was about 90% initially after fertilization treatments started (1990–1991), then

declined to around 70% with continued N additions (2002). That N retention by a forest would increase after additions of more N is contrary to current understanding of N saturation.

Some of this lack of fit with N saturation conceptual models may be due to a greater resistance of hardwood/deciduous forests to N saturation relative

Fig. 2 Volume-weighted mean concentrations for soil solution of Ca, Mg, K, SO_4 , NO_3 and pH by soil horizon from WS3 (*open squares*) and WS4 (*closed circles*), with *trend line overlaid*, Fernow Experimental Forest, West Virginia, USA. *Vertical bar* represents start of the ammonium sulfate fertilizer additions to WS3



to conifers. Larger pools of nutrients are cycled via annual litterfall in deciduous systems, resulting in different rates and processing of N. Research from Bear Brook Watershed in Maine (Fernandez, Rustad, Norton, Kahl, & Cosby, 2003) and elsewhere (Fenn et al., 1998) provides at least some support for the relatively greater sensitivity of conifer ecosystems to N saturation and acidification. Also, the timing of the fertilizer applications to WS3 may not be the

most opportune for plant uptake and growth stimulation. In forest management applications, to maximize growth response, fertilizer would normally be applied around bud break in the spring. Much of the total N loading (43%) from both ambient deposition and the fertilizer treatment occurred in the 8-month period from September to May when vegetation was mostly dormant. About 80% of the nitrate was exported in stream water from the

fertilized watershed between December and May. Thus, the question arises whether WS3 is saturated with N throughout the year, or is responding to chronic N deposition and artificial N inputs by leaching N during periods that do not coincide with high biotic demands. Clearly, there is a need for an improved understanding, both temporally and spatially, of N dynamics and N saturation in temperate deciduous forest ecosystems.

3.3 Base Cation Leaching

Evidence exists that the fertilization treatment has affected the cycling of base cations, particularly calcium (Ca), within WS3. Soil solution concentrations of Ca and magnesium (Mg) increased during the early years of treatment, and then decreased in the later years of the study (Fig. 2). This pattern of base cation increases and decreases also was evident in stream water during peakflow, but was less obvious in stream water concentrations at baseflow (Edwards et al., 2006), although significant increases in stream water baseflow concentrations and exports of base cations were observed during the first few years of treatment (Fig. 1), consistent with acidification models (Fernandez et al., 2003; Galloway et al., 1983; Norton & Fernandez, 1999; Norton et al., 2003). This pattern can be interpreted as a cycle of

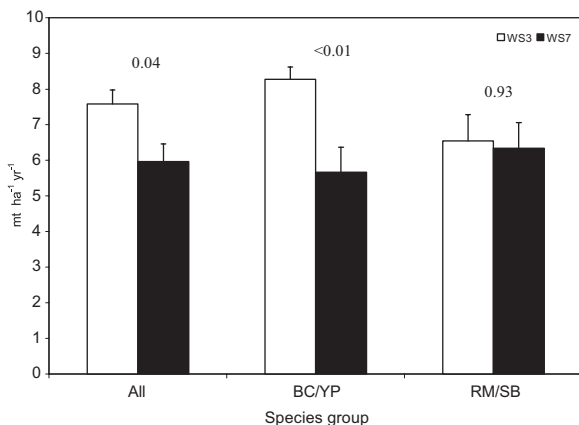


Fig. 3 Mean net annual (1990–2004) biomass production by trees on growth plots, WS3 (open bars) and WS7 (dark bars), Fernow Experimental Forest, West Virginia, USA. Plots were stratified by a higher occurrence of *black cherry*/yellow-poplar (BC/YP) or *red maple*/sweet birch (RM/SB). Numbers above means are significance levels, indicating probability > *F* statistic for each comparison

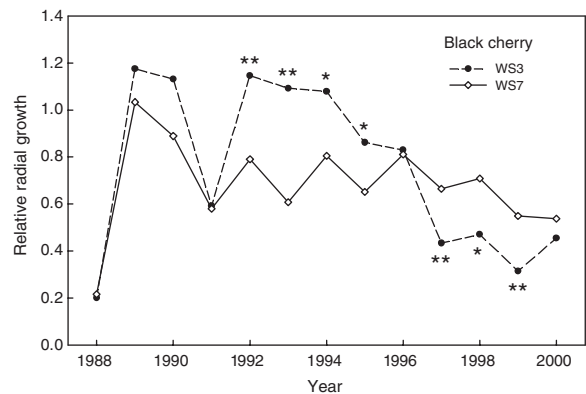


Fig. 4 Relative radial growth patterns for 10 *black cherry* trees on WS3 (dashed line) and WS7 (solid line), Fernow Experimental Forest, West Virginia, USA, during acidification treatments which began in 1989. Asterisks by year indicate significant differences; * $\alpha=0.1$, ** $\alpha=0.05$. (From DeWalle et al., 2006)

increasing base cation mobility, followed by depletion of available base cations from the soil exchange sites as hypothesized by Norton et al. (2003). Patterns of tree ring chemistry and radial growth of some tree species are approximately concurrent with the trends of mobilization and depletion observed in the soil water chemistry (Fig. 4). However, no significant decreases in soil base cation concentrations or soil base saturation were detected. Nor were any obvious signs of tree decline (crown dieback, mortality.) observed.

4 Conclusions

During the first 15 years of the Fernow Watershed Acidification Study, much has been learned; the processes of acidification, N saturation and base cation leaching have been documented as a result of the treatments. As treatment of WS3 has continued, we have found that some conceptual models have been useful in predicting responses, while others do not seem to “fit” the deciduous hardwood forest ecosystem of WS3. The central hardwood forest type is one of the most widespread in the United States (Adams, Burger, Jenkins, & Zelany, 2000), and therefore we need to better understand the effects of atmospheric deposition on these important forest ecosystems. Continuation of the Fernow Watershed Acidification Study will help address this need.

Acknowledgements This experiment was planned and conducted largely by personnel of the USDA Forest Service, Northeastern Research Station at Parsons, West Virginia, USA, with initial funding from the US Environmental Protection Agency. Subsequent support by the USDA Forest Service Northern Global Change Program, and the National Science Foundation's Long-term Research in Environmental Biology Program are also acknowledged.

References

- Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., et al. (1998). Nitrogen saturation in temperate forest ecosystems: Hypotheses revisited. *Bioscience*, 48, 921–934.
- Adams, M. B. (1999). Acidic deposition and sustainable forest management in the central Appalachians, USA. *Forest Ecology and Management*, 122, 17–28.
- Adams, M. B., Burger, J. A., Jenkins, A. B., & Zelazny, L. (2000). Impact of harvesting and atmospheric pollution on nutrient depletion of eastern US hardwood forests. *Forest Ecology and Management*, 138, 301–319.
- Adams, M. B., DeWalle, D. R., & Hom, J. (Eds.) (2006). *The Fernow watershed acidification study* (p. 290). Berlin Heidelberg New York: Springer.
- Adams, M. B., Kochenderfer, J. N., Wood, F., Angradi, T. R., & Edwards, P. J. (1994). *Forty years of hydrometeorological data on the Fernow Experimental Forest, West Virginia*. USDA Forest Service General Technical Report NE-184. Radnor, PA. 24 p.
- Core, E. L. (1966). *Vegetation of West Virginia* (p. 217). Parsons, WV: McClain.
- DeWalle, D. R., Kochenderfer, J. N., Adams, M. B., Miller, G. W., Gilliam, F. S., Wood, F., et al. (2006). Vegetation and acidification. In M. B. Adams, D. R. DeWalle, & J. Hom (Eds.), *The Fernow watershed acidification study* (pp. 137–188). Berlin Heidelberg New York: Springer.
- Edwards, P. J., Williard, K. W. J., Wood, F., & Sharpe, W. E. (2006). Soil water and stream water chemical responses. In M. B. Adams, D. R. DeWalle, & J. Hom (Eds.), *The Fernow watershed acidification study* (pp. 71–136). Berlin Heidelberg New York: Springer.
- Edwards, P. J., & Wood, F. (1993). *Fernow experimental forest watershed acidification project: Field and laboratory quality assurance/quality control protocols*. USDA Forest Service General Technical Report NE-177. Radnor, PA 15 p.
- Fenn, M. E., Poth, M. A., Aber, J. D., Baron, J. S., Bormann, B. T., Johnson, D. W., et al. (1998). Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. *Ecological Applications*, 8, 706–733.
- Fernandez, I. J., Rustad, L. E., Norton, S. A., Kahl, J. S., & Cosby, B. J. (2003). Experimental acidification causes soil base-cation depletion at the Bear Brook Watershed in Maine. *Soil Science Society of America Journal*, 67, 1909–1919.
- Galloway, J. N., Norton, S. A., & Church, M. R. (1983). Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model. *Environmental Science & Technology*, 17, 541A–545A.
- Gilliam, F. S., Yurish, B. M., & Adams, M. B. (2001). Temporal and spatial variation of nitrogen transformations in nitrogen saturated soils of a central Appalachian hardwood forest. *Canadian Journal of Forest Research*, 31, 1768–1785.
- Helvey, J. D., & Kunkle, S. H. (1986). *Input–output budgets of selected nutrients on an experimental watershed near Parsons, West Virginia*. USDA Forest Service General Technical Report NE-584. Broomall, PA. 7 p.
- Lynch, J. A., Bowersox, V. C., & Grimm, J. W. (2000). Changes in sulfate deposition in eastern USA following implementation of phase I of Title IV of the Clean Air Act Amendments of 1990. *Atmospheric Environment*, 34(11), 1665–1680.
- Madarish, D. M., Rodrigue, J. L., & Adams, M. B. (2002). *Vascular flora and macroscopic fauna on the Fernow Experimental Forest, USDA Forest Service*. General Technical Report NE-291. Newtown Square, PA. 37 p.
- May, J. D., Burdette, S. B., Gilliam, F. S., & Adams, M. B. (2005). Interspecific divergence in foliar nutrient dynamics and stem growth in response to excessive nitrogen deposition in a temperate forest. *Forest Ecology and Management*, 35, 1023–1030.
- Norton, S. A., & Fernandez, I. J. (Eds.) (1999). *The Bear Brook Watershed in Maine: A paired watershed experiment – The first decade (1987–1997)*. Boston, MA: Kluwer.
- Norton, S. A., Fernandez, I. J., Kahl, J. S., & Reinhardt, R. L. (2003). Acidification trends and the evolution of neutralization mechanisms through time at the Bear Brook Watershed in Maine (BBWM). *Water, Air, & Soil Pollution. Focus*, 4, 289–310.
- Pan, C., Tajchman, S. J., & Kochenderfer, J. N. (1997). Dendroclimatological analysis of major forest species of the central Appalachians. *Forest Ecology and Management*, 98, 77–87.
- Patric, J. H., & Goswami, N. (1968). Evaporation pan studies – Forest research at Parsons. *West Virginia Agriculture and Forestry*, 1(4), 6–10.
- Peterjohn, W. T., Adams, M. B., & Gilliam, F. S. (1996). Symptoms of nitrogen saturation in two central Appalachian hardwood forest ecosystems. *Biogeochemistry*, 35, 507–522.
- Reuss, J. O., & Johnson, D. W. (1986). *Acid deposition and the acidification of soils and waters* (p. 119). Berlin Heidelberg New York: Springer.
- Stoddard, J. L. (1994). Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. In L. A. Baker (Ed.), *Environmental chemistry of lakes and reservoirs. Advances in chemistry series*, vol. 237 (pp. 223–284). Washington, DC: American Chemical Society.
- Venterea, R. T., Groffman, P. M., Castro, M. S., Verchot, L. V., Fernandez, I. J., & Adams, M. B. (2004). Soil emission of nitric oxide in two forest watershed subjected to elevated N inputs. *Forest Ecology and Management*, 196, 335–349.

Response of Drinking-water Reservoir Ecosystems to Decreased Acidic Atmospheric Deposition in SE Germany: Signs of Biological Recovery

Andreas Meybohm · Kai-Uwe Ulrich

Received: 6 July 2005 / Accepted: 3 April 2006 / Published online: 11 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Strongly decreasing atmospheric emissions and acidic deposition during the 1990s have initiated chemical reversal from acidification in several drinking-water reservoirs of the Erzgebirge, SE Germany. We studied responses of phytoplankton, zooplankton and fish stocks in five reservoirs and at enclosure scale after experimental neutralization of 1,200 m³ of lake water. About 4 months after this treatment, diatoms and cryptomonads replaced the predominating chrysophytes and dinoflagellates. The colonization by acid-sensitive species of green algae, cryptomonads, rotifers and Cladocera (e.g. *Bosmina longirostris*) is explained by the occurrence of dormant stages or by survival of individuals in very low abundances. Analogous to the enclosure experiment, three reservoirs showed significantly ($p < 0.01$) falling trends of chlorophyll *a* and phytoplankton biovolume, mainly due to the decline of dinoflagellates. Picoplankton and diatoms increased slightly in two reservoirs. The zooplankton communities were

dominated by rotifers and small Cladocera. Representatives of the genus *Daphnia* were lacking. Two reservoirs were re-colonized by zooplanktivorous fish populations of either perch (*Perca fluviatilis*) or sunbleak (*Leucaspis delineatus*). The latter exhibited extremely high fluctuating abundance and biomass and even suffered from a population crash. This natural mortality was caused by a limited food supply. Hence, severe top-down control may delay the recovery of larger zooplankton species like daphnids. Fishery management comprising the introduction of predatory fishes can help to control zooplanktivorous fish populations and to prevent their mass mortality.

Keywords acidification reversal · enclosure experiment · fish stock · phytoplankton · recovery · reservoir ecosystem · zooplankton

1 Introduction

Atmospheric acidification has caused severe damages to aquatic communities in many siliceous mountain ranges of central Europe, for instance in the Black Forest, Harz, Erzgebirge and Bohemian Forest. Lake ecosystems have lost their food web complexity and stability due to reduced biodiversity. Larger zooplankton species have vanished and the extinction of fish stocks has led to a reduced number of trophic levels. On the other hand, Dinophyceae and Chrysophyceae

A. Meybohm (✉)
Landestalsperrenverwaltung Sachsen,
Investigation Center Plauen,
Baerenstrasse 46, D-08523 Plauen, Germany
e-mail: Andreas.Meybohm@ltv.smul.sachsen.de

K.-U. Ulrich
Forschungszentrum Rossendorf e.V.,
Institute of Radiochemistry,
Dresden, Germany

(e.g., *Synura* species) increased to high abundances (Almer, Dickson, Ekström, Hörnström, & Miller, 1974). Most of these organisms are undesired with respect to drinking-water treatment because they produce odorous substances and move actively through filter systems (Keitel, 1995). In Saxony (Germany), about two million people are supplied with drinking-water from reservoirs. This purpose requires intensive monitoring of the water quality in the reservoirs and their main tributaries, executed by the Dam Administration of Saxony State.

Chemical data for 22 acidified tributaries and seven reservoirs in the Erzgebirge from 1993 to 2003 revealed distinct trends of acidification reversal (Ulrich, Paul, & Meybohm, 2006). The abatement of air pollution was considered to be the decisive factor causing this rapid and extensive reversal of acidification. The strong decrease of acidity and toxic forms of aluminum (Al) provides improved habitat quality for the recovery of sensitive aquatic organisms. Evidence of natural recovery of aquatic communities from acidification is rarely described in the literature (Keller, Yan, Somers, & Henneberry, 2002). In central Europe, first responses have been reported from the Bohemian Mountains (Czech Republic) (Vrba et al., 2003). The phytoplankton biomass and rotifer abundance increased in one lake, and a population of *Ceriodaphnia quadrangula* (Cladocera) returned into the pelagic zone of another lake. Recently, Tammi, Rask, Vuorenmaa, Lappalainen, and Vesala (2004) ascribed the increasing catches of perch and their successful reproduction to the improved water quality of small Finnish lakes.

The aim of this paper is to examine the evidence of biological recovery in reservoir ecosystems from both field and experimental studies, and to discuss aspects that are relevant for reservoir management practices.

2 Site Description

We studied five acidified reservoirs of the Erzgebirge (Ore Mountains) located at an altitude of 562–904 m above sea level, namely the reservoirs Werda (WD), Muldenberg (MB), Carlsfeld (CF), Sosa (SO) and Falkenstein (FA). Lake area and mean depth range between 0.13–0.92 km² and 6.3–15.2 m, respectively. Mean water retention times vary between 0.2 and 0.7 years. The reservoirs are neither connected to non-

acidified lakes nor to downstream rivers due to the dam barrier. The watersheds of the monitored headwaters are small (0.5–10 km²) and exhibit different degrees of acidification and reversal. For more information see Ulrich et al. (2006).

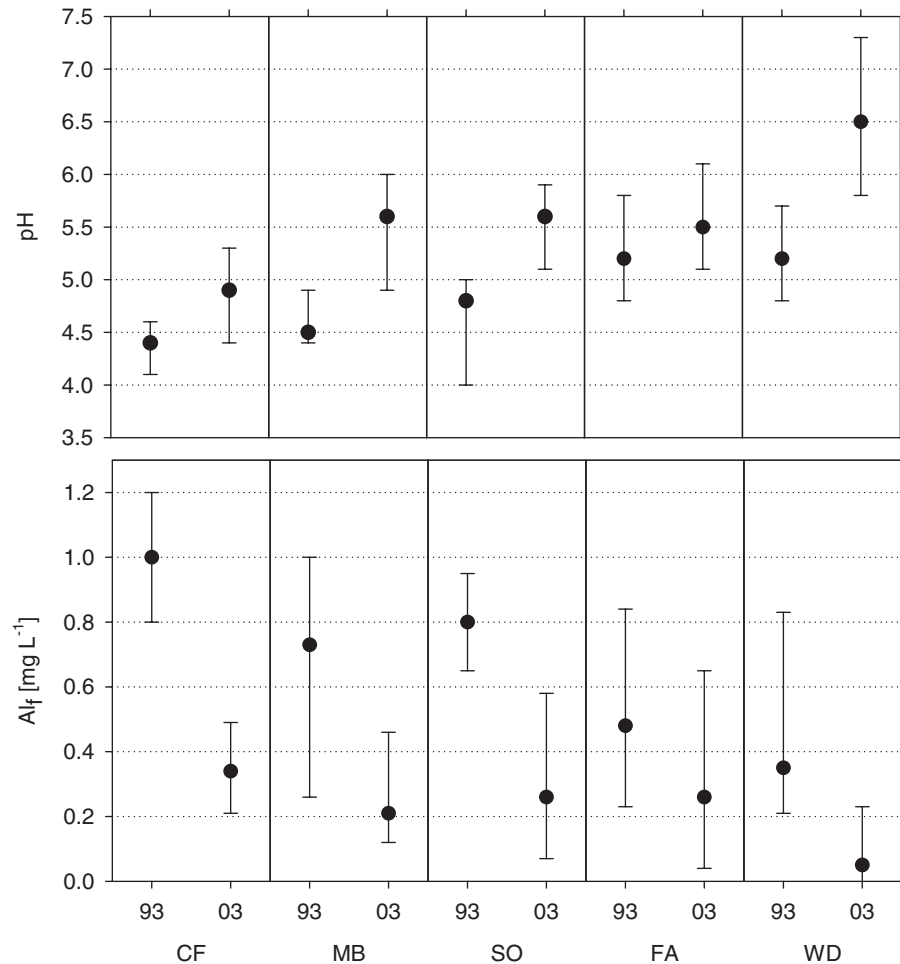
Few historical data regarding water quality and biology exist. The reservoirs CF, FA, SO were affected by acidification since their start-up, the other two were neutral before being acidified. The water quality of WD allowed a stocking with salmonids shortly after the start-up. Due to the progression of atmospheric acidification, the fishery was abandoned around 1955, and fish became extinct by the beginning of the 1960s. Despite the slightly humic water quality of SO, 1,500 individuals of rainbow trout (*Salmo gairdnerii*) and brook trout (*Salvelinus fontinalis*) were introduced in 1954. No fish were caught two years later despite high fishing efforts. Hence, acidification already hindered fish from survival and reproduction in the 1950s. Native and managed fish populations survived in the non-acidified, but sensitive reservoirs Neunzehnhain II (NH) and Cranzahl (CR), which therefore represent reference lakes for our study.

Since about 1993, the acidified reservoirs show significant patterns of chemical reversal from acidification (Ulrich et al., 2006), illustrated by pH increase and substantial decline of dissolved Al concentrations (Fig. 1). However, in 2003 pH values <6 and Al³⁺ concentrations >0.2 mg l⁻¹ still occurred in these reservoirs except WD, thus limiting the habitat quality. The FA reservoir, which exhibited a minor change of its chemical composition, served for an in-situ enclosure experiment to investigate initial effects of acidification reversal on water chemistry and plankton community (see below).

3 Materials and Methods

Long-term data on chlorophyll concentrations and phytoplankton biovolumes were collected at least monthly from August 1994 to December 2003 within the ice-free season. Statistical trend analysis was carried out by the nonparametric Seasonal Kendall Test (Gilbert, 1987; Hirsch & Slack, 1984; Hirsch, Slack, & Smith, 1982) according to Libiseller (2002). The zooplankton community was studied irregularly in FA, MB, SO and CF, and monthly in NH and WD

Fig. 1 Ranges of pH and aluminum concentration (0.45 μm filtered fraction) of the studied reservoirs given by minimum, maximum and mean values of the years 1993 and 2003



from May 2000 to December 2003. During the enclosure experiment in FA (see below) phyto- and zooplankton were sampled every 2 weeks.

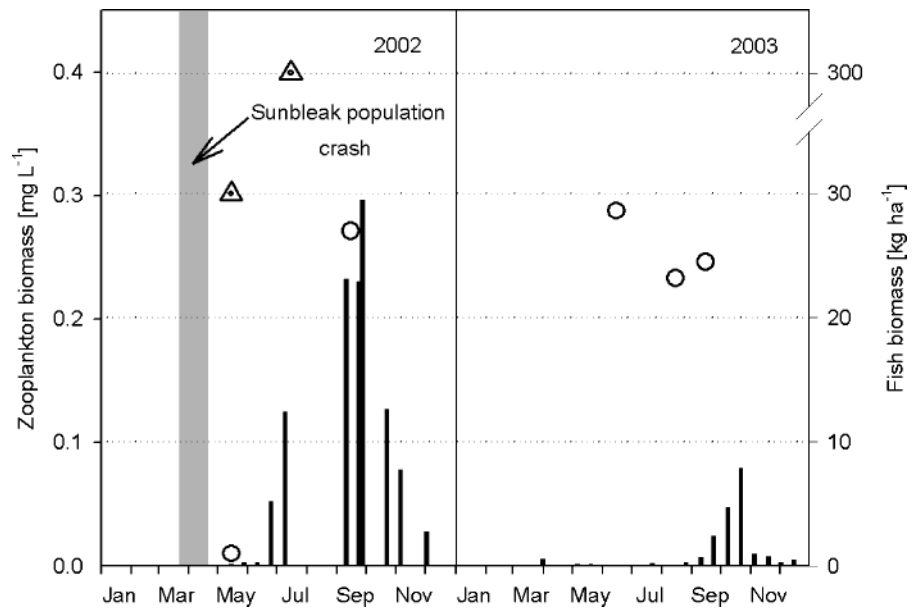
Water samples from the trophogenic zone of the reservoirs and the enclosure column were gained by a Ruttner sampling device and fixed with Lugol's solution. Zooplankton nets with mesh size of 50 and 250 μm (55 and 170 μm for enclosure sampling) were used to sample rotifer and mesozooplankton individuals, respectively. The phytoplankton biovolumes and the wet weight biomass of zooplankton were determined according to Hoehn et al. (1998).

Investigation of the fish stocks of WD was carried out in 2002 and 2003 using gill nets, beach seines and ring seines (Appelberg, Bergquist, & Degerman, 2000), electro-fishing (Foote, Knudsen, Vestnes, MacLennan, & Simmonds, 1987) and echo sounding (SIMRAD EY500 split beam) according to McLennan and Simmonds (1992). The fish stocks of

MB were studied concomitantly with total reservoir drainage due to the dam restoration in December 2004. We calculated the condition factor (Bangenal & Tesch, 1978) from measured body mass and length of individual fish. The stomach content of $n=140$ individuals was examined in addition.

In order to study biological effects of acidification reversal by treatment of acidic lake water with an innovative buffering substance, research took place at FA reservoir from 1998 to 2001 (Ulrich et al., 2001). Two enclosures were installed: one for the experiment (referred to as experimental enclosure, EE), and another serving as untreated reference (RE). Each of them measured 10 m in diameter and 19 m by depth, enclosing a water volume of $\sim 1,200 \text{ m}^3$. The buffering substance was a pulverized mixture containing NaHCO_3 , CaCl_2 , Na_2CO_3 , and $\sim 1\%$ CaCO_3 . The dose of each component was precisely adjusted on the lake water chemistry to achieve rapid de-

Fig. 2 Zooplankton biomass on wet weight basis (black bars, left ordinate) and sunbleak biomass (right ordinate) estimated by electro-fishing in the littoral zone (triangles), and by echosounding and seining in the pelagic zone (circles) of WD reservoir in 2002 and 2003



acidification, instantaneous increase of the buffering capacity, and the target pH stabilized around 6.7. In contrast to the application of limestone or soda, this mixture prevents pH values higher than ~8.2 due to an intrinsic buffering process (Willuweit, Weißgräber, Belouschek, & Lönz, 1995). After a dose of 43 g m^{-3} has been applied to the EE, the monitoring period covered eight months including chemical water analyses (Ulrich et al., 2006; Ulrich et al., 2001) and plankton analyses as described above.

4 Results

4.1 Trends of Phyto- and Zooplankton

The chlorophyll *a* concentrations and phytoplankton biovolumes significantly ($p < 0.01$) decreased in FA, MB and SO between 1994 and 2003. This resulted from significantly declining biovolumes of dinoflagellates, which comprised ~80% of the phytoplankton. Dominating species were *Peridinium umbonatum* and *Gymnodinium uberrimum*. Increasing trends were observed for the autotrophic picoplankton in WD ($p < 0.05$) and for diatoms in WD ($p < 0.05$) and MB ($p < 0.01$). Chrysophyceae, Cryptophyceae, Chlorophyceae and Cyanobacteria showed no trends.

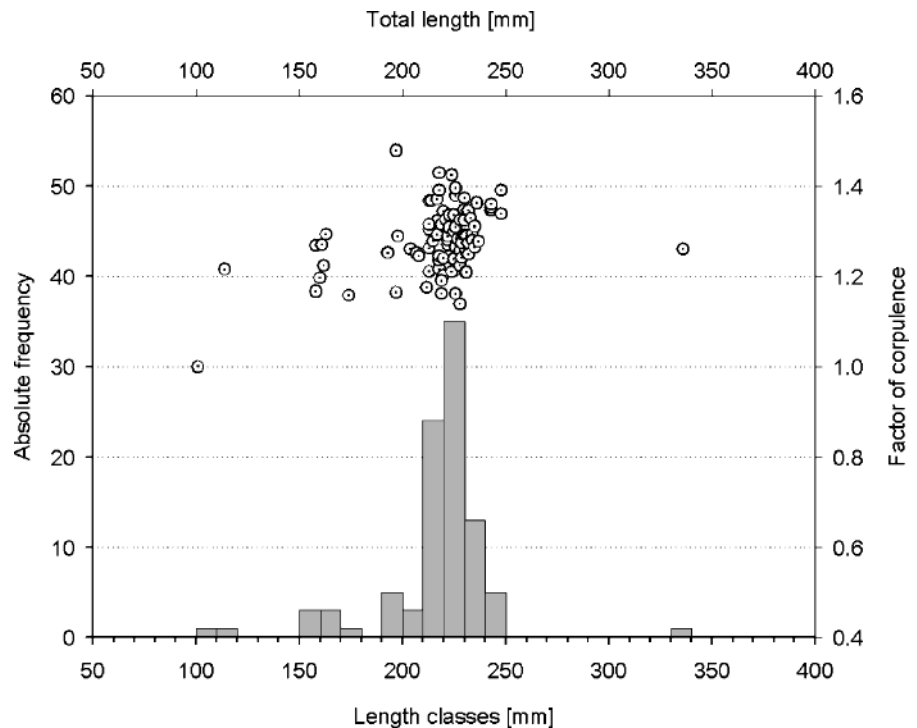
The micro- and mesozooplankton community mainly consisted of rotifers (*Asplanchna* spp, *Kera-*

tella spp, *Synchaeta* sp., *Polyarthra* sp., *Trichocerca* sp., *Brachionus* sp., *Pompholyx* sp., *Lecane* sp.), copepods (predominantly cyclopoids, e.g. *Acanthocyclops robustus* in FA reservoir) and small Cladocera (*Ceriodaphnia quadrangula*, *Bosmina longirostris*, *Chydorus sphaericus*, and *Alona* sp.). Comparing the mesozooplankton composition, the reservoirs WD and FA were more densely populated by small Cladocera like *Alona*, *Bosmina* and *Ceriodaphnia* than MB and CF. The genus *Daphnia* was lacking in all of these reservoirs except NH and CR. Larvae of *Chaoborus* sp. were temporarily common in very low abundances in FA, MB, WD and CF. In addition, CF and SO were densely populated by different species of Corixidae, mainly *Arctocorisa germari*, *Callicorixa praeusta* and *Glaenocorisa propinqua*. This was likely due to the absence of fish. Trends in the zooplankton community were not detectable.

4.2 Recolonization of Fish

As opposed to SO and CF, where the early stage of acidification reversal was not yet followed by a recolonization of fish, small individuals were recognized in WD in 1999. Two years later, large shoals of sunbleak (*Leucaspis delineatus*) appeared. In May 2002, the fish shoals disappeared and huge amounts of dead fish were found on the shore. A quantitative study showed that the fish biomass remaining after

Fig. 3 Length distribution (grey bars on the lower abscissa and left ordinate) and condition factor (dotted circles on the upper abscissa and right ordinate) of perch in MB reservoir 2004



the crash was low, yielding 1 and 30 kg ha⁻¹ (1,000 and 67,000 individuals ha⁻¹) in the pelagic and the littoral zone, respectively (Fig. 2). The population mainly consisted of individuals of the 1⁺ age class. Due to successful reproduction, the fish biomass augmented to 27 and 300 kg ha⁻¹ in the pelagic and the littoral zone, respectively, a few months later. In 2003, the pelagic sunbleak biomass ranged from 23 to 29 kg ha⁻¹ between June and September, but no population crash happened.

In the MB reservoir, a limited number of small perch (*Perca fluviatilis*) was observed for the first time in 2002 and then consistently appeared in the littoral zone. Perch dominated the yield of 50 kg that was fished concomitantly with total reservoir drainage in December 2004. In addition, two individuals of pike (*Esox lucius*) and one eel (*Anguilla anguilla*) were caught. The size distribution of perch showed dominance of a peak cohort between 200 and 250 mm (Fig. 3). Only very few young of the year individuals and older individuals were caught. Stomach analyses indicated cannibalism of the older individuals. The younger perch consumed benthos, water bugs and different kinds of insect larvae. The calculated condition factors range slightly below typical average

values and thus illustrate quite good feeding conditions, but the intestinal fat content was extremely low.

The feeding conditions in WD were worse as compared to MB reservoir. This was reflected by most of the sunbleak individuals showing extremely low condition factors between 0.58 and 0.95. Gut analyses revealed high proportions of *Ceriodaphnia*, *Bosmina* and copepods from the pelagic zooplankton community. Moreover, sunbleak consumed terrestrial and aquatic insects, phytoplankton and occasionally high amounts of spruce pollen.

4.3 Enclosure Experiment

The treatment of the EE by adding buffering material substantially changed the water chemistry (Table 1). Within 30 min after the dosage, the alkalinity increased by a factor of 9, and the pH rose from 4.95 to 6.6. Both parameters were stable throughout the experiment. The initially high amounts of iron and aluminum passing a 0.45 µm filter (referred to as Fe_f and Al_f) transformed into colloids and aggregates of which ~90% settled within the first week. The UV absorption of water (UV abs. at 254 nm), considered

Table 1 Water composition of the experimental enclosure before and after the supply of 43 g m^{-3} of a special buffering substance (Ulrich et al., 2001)

Parameter	Before treatment	After 30 min	After 7 days	After 6 months
PH	4.95	6.6	6.7	6.7
Alkalinity mM	0.05	0.44	0.38	0.42
UV, abs., m^{-1}	7.31	3.74	3.78	3.07
Al_t , mg l^{-1}	1.35	1.23	0.14	0.01
Al_f , mg l^{-1}	1.2	0.03	0.03	0.01
Fe_t , mg l^{-1}	0.18	0.18	0.02	<0.01
Fe_f , mg l^{-1}	0.08	<0.01	<0.01	<0.01
Mn_t , mg l^{-1}	0.48	0.47	0.48	0.02
Mn_f , mg l^{-1}	0.48	0.47	0.48	0.02
P_t , $\mu\text{g l}^{-1}$	10.4	11.3	4.1	3.8
P_f , $\mu\text{g l}^{-1}$	1.3	<1	<1	1.2

The indices *t* and *f* indicate total and 0.45 μm filtered fractions.

as an estimate for dissolved organic (humic) substances, halved within 30 min (Table 1). This indicated co-precipitation of organic matter with hydrolyzed Al and Fe oxyhydroxides. The concentration of filter-passing manganese (Mn_f) showed no reaction within the first 5 weeks, but then started to decline slowly, most likely due to microbial induced oxidation and subsequent settling (Ulrich et al., 2001). After 6 months, the concentrations of total iron (Fe_t) and Fe_f were $<0.01 \text{ mg L}^{-1}$, those of Al_t and Al_f amounted to 0.01 mg l^{-1} , and those of Mn_t and Mn_f were 0.02 mg l^{-1} , thus being below the thresholds of the German Drinking-Water Directive. Even total phosphorus (P_t) exhibited only one third of its initial concentration (Table 1). Furthermore, trace metals like Zn, Ni, Co and Cd settled out of the water column. Hence, toxic metals were successfully removed from the EE.

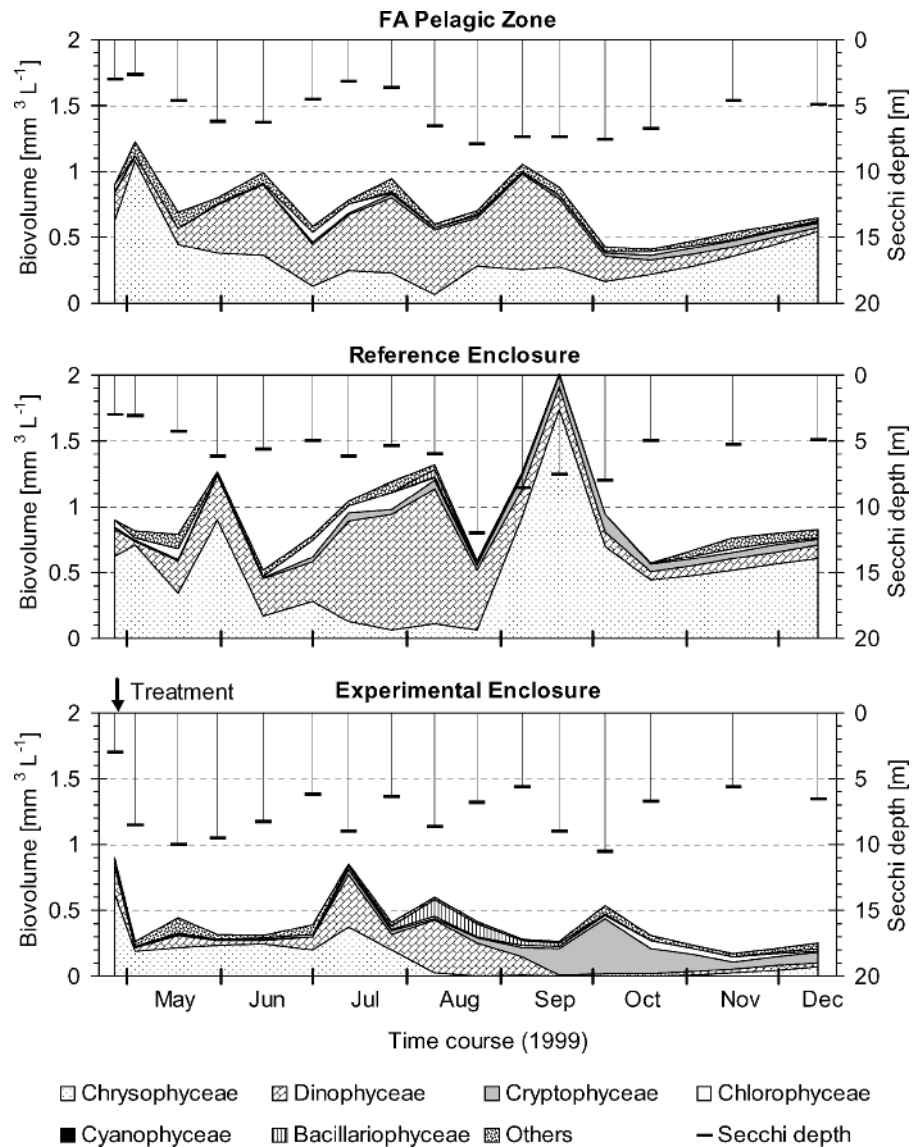
Within 1 week after the EE treatment, the phytoplankton biovolume dropped to one third of its initial value, likely due to co-precipitation (Fig. 4). The Secchi depth rose up to 10 m. The chlorophyll *a* concentration and phytoplankton biomass remained low throughout the study period. Four months after the treatment, chrysophytes and dinoflagellates, which prevailed in the pelagic zones of RE and FA, were substituted by diatoms and cryptomonads in the EE. In addition, new phytoplankton species appeared: the diatoms *Rhizosolenia eriensis* and *Navicula* sp., the green algae *Ankistrodesmus falcatus* and *Oocystis* sp., and the cryptomonad *Rhodomonas minuta* (Freier & Bollenbach, 2001). The zooplankton biomass of the RE and FA pelagic zone reached up to 0.7 mg l^{-1} during summer and fall 1999. It was much lower in

the EE, $<0.1 \text{ mg l}^{-1}$ in summer and $\sim 0.35 \text{ mg l}^{-1}$ during fall season. Whereas the cladoceran *Ceriodaphnia quadrangula* dominated at the three sites, *Bosmina longirostris* and three rotifer species (*Keratella quadrata*, *K. cochlearis* and *Kellicottia* sp.) were observed only in EE. The biomass of ciliates, rotifers and copepods remained low. The cladoceran *Chydorus sphaericus*, which had not been found in the FA pelagic zone, appeared in both enclosures, thus probably reflecting altering influences of the enclosures themselves on the plankton community.

5 Discussion

One of the main questions of research on the effects of anthropogenic acidification and its reversal is whether the biological damage is fully reversible. Today, there is already evidence from neutralization of acidified lakes in Ontario, Canada (Dillon, Yan, Schneider, & Conroy, 1979) and from lake liming in Scandinavia, that the phytoplankton diversity re-increases and the acidification-induced dominance of Dinophyceae decreases (Eriksson, Hörnström, Mossberg, & Nyberg, 1983; Hultberg & Andersson, 1982; Niinioja, Ahtiainen, & Holopainen, 1990). The decreasing trends of Dinophyceae biovolumes in three reservoirs are in accordance with these findings. In the WD reservoir, the Dinophyceae did not decline, but we observed rising trends of picoplankton and diatoms. The latter effect was also reported from other lakes (Hultberg & Andersson, 1982). In contrast to our results, Schaumburg (2000) could not detect signifi-

Fig. 4 Temporal patterns in phytoplankton biovolume (left ordinate) and Secchi depth (right ordinate) comparing the FA pelagic zone with reference and experimental enclosure, the water of which was neutralized by dosing 43 g m^{-3} of a special buffering substance (indicated by arrow)



cant changes of the phytoplankton community in Bavarian forest lakes.

The appearance of new phytoplankton and zooplankton species such as *Rhodomonas minuta*, *Oocystis* sp., *Ankistrodesmus falcatus*, *Keratella* sp., *Kellicottia* sp., and *Bosmina* sp. in the enclosure experiment is attributed to the development of acid-sensitive species from dormant stages (Freier & Bollenbach, 2001). Another explanation for rapid colonization is that many plankton species adapted to oligotrophic conditions are able to survive and to reproduce in moderately acidic conditions, but in abundances too low to be detected by conventional

sampling (Fott, Prazakova, Stuchlik, & Stuchlikova, 1994).

Similar to the recovery trends of phytoplankton, the chemical reversal from lake acidification resulted in a higher zooplankton diversity (Keller et al., 2002). Due to lack of data of the time before acidification and due to the relatively short investigation period, alterations of the zooplankton community are not detectable in WD reservoir. Despite pH values >6.0 in the summer season, pH regularly dropped down to 5.5 during the snowmelt. The lack of *Daphnia* while occurrence of *Ceriodaphnia* indicates an early stage of recovery of the zooplankton community in WD

(Degerman, Henrikson, Herrmann, & Nyberg, 1994; Vrba, Kopacek, & Fott, 2000). This is supported by an extremely high intra-annual variability of the zooplankton biomass (median ~120%, quartiles of 98 and 180%). The variability is much lower in NH (median ~100%, quartiles of 80 and 140%) and in the Dröda reservoir (median ~70%, quartiles of 60 and 73%), a non-acidified, eutrophic drinking-water reservoir with high biodiversity and well balanced food web. Episodically acidic lakes show a very limited biodiversity in all trophic levels and are far away from ecological equilibrium, reflected by a high intra-annual variation of the zooplankton biomass. In regard to this variability, the acid-sensitive NH reservoir ranges between WD and Dröda due to its near-neutral pH and its native fish population including both predatory and prey species. (Holt & Yan, 2003) pointed out that the recovery of zooplankton in the Sudbury lakes (Canada) took more than a decade at conditions of $\text{pH} > 6.0$. Similar conditions were observed only in the WD reservoir.

Many fish stocks of acid-sensitive lakes in central Europe were damaged or even lost due to atmospheric acidification (Schaumburg, 2000; Vrba et al., 2000). In SO and CF the extinction of fish was confirmed by intense fishing and total reservoir drainage. The appearance of sunbleak in WD is most likely due to re-colonization from unknown origin. Headwater streams of our study can be ruled out as refuges for pelagic fish species because they were more acidic and loaded by toxic Al species than the reservoirs, and fish stocking did not take place. The access to downstream refuges is blocked by dams. However, survival of older perch cannot be excluded in the MB reservoir because perch are more acid-tolerant than cyprinids like roach and sunbleak. Perch survived in many Scandinavian lakes affected by acidification (Tammi et al., 2003). First signs of recovered perch populations in Finland were visible from high abundance of young of the year cohorts (Nyberg, Vuorenmaa, Rask, Mannio, & Raitaniemi, 2001) and increasing CPUE and lower mean body weights (Tammi et al., 2004).

The extent of phytoplankton recovery depends on the grazing pressure of herbivorous zooplankton which itself may be regulated by predation of fish (Keller & Yan, 1998; Schindler et al., 1991). The dense sunbleak population in WD exerts a high predation pressure on the zooplankton community,

in particular on the crustaceans. The relatively stable biomass of sunbleak (30 kg ha^{-1}) suggests that the actual carrying capacity of zooplanktivorous fish has been reached or even exceeded. This estimation is supported by an extremely low zooplankton biomass $< 0.3 \text{ mg l}^{-1}$ (Fig. 2) and by a low condition factor of the sunbleak individuals, ranging between 0.58 and 0.95. These low values reflect limited energy supply, extremely high degree of utilization of food resources (i.e. zooplankton), and high intraspecific competition. Hence the sunbleak biomass was restricted by food supply. Due to a certain time delay of this negative feedback mechanism, the course of biomass exhibits high amplitudes that are characteristic for ecosystems with low diversity. The introduction of predatory fish species could help to control the sunbleak population and to prevent increased natural mortality due to mass reproduction and excessive utilization of food resources.

Physical, chemical and biological characteristics determine the suitability of surface waters for a drinking water supply. Phytoplankton exerts a high influence on the extent and costs of raw water treatment. Such treatment requires additional efforts in the elimination of chrysophytes since these algae actively move through the filters using their flagellum, and since they produce odorous substances (dimethyldisulfide, 2,6-nonadienal) which have to be removed by ozone and charcoal. Though this study could not detect rising trends of chrysophytes either in the investigated reservoirs or in the enclosure experiment, increasing abundance of this group is expected from other studies on the recovery of phytoplankton (Dillon et al., 1979; Niinioja et al., 1990). Given the rising trend of picoplankton in WD, the elimination of small spherical cells requires higher doses of a flocculant. Substantial increases of both chrysophytes and picoplankton would increase the expenditure of drinking water treatment. On the other hand, the water treatment benefits from the recovery of filter feeding crustaceans such as *Daphnia*, which would improve biofiltration. This implies both stocking with piscivorous fish to reduce zooplankton predation, and ongoing reduction of acid and toxic metal input. As soon as reservoirs are re-colonized by fish, the application of a targeted fisheries management is necessary to accelerate the process of zooplankton recovery and to prevent natural crashes of fish populations in the early stage of recovery. Moreover, the increase of biodiversity favors planktonic succes-

sion of many more species of algae that may interfere with the raw water treatment. Therefore, extensive limnological surveys become an even more important base of operative management practices in drinking-water reservoirs.

Acknowledgements Data used in this paper are derived from the self-monitoring program of the Dam Administration of Saxony State. K. Freier and M. Bollenbach investigated the plankton within the scope of the enclosure experiment that benefited from support of the Federal Ministry of Education, Science and Technology (BMBF) under Contract No. 02WT9841/3. Investigation of fish stocks in WD reservoir was carried out by M.-G. Werner on behalf of the Dam Administration of Saxony State. We thank H. C. Naess and two anonymous referees for useful comments.

References

- Almer, B., Dickson, W., Ekström, C., Hörnström, E., & Miller, U. (1974). Effects of acidification on Swedish lakes. *Ambio: A Journal of the Human Environment*, 3, 30–36.
- Appelberg, M., Bergquist, B. C., & Degerman, E. (2000). Using fish to assess environmental disturbance of Swedish lakes and streams – a preliminary approach. *Verh. Internat. Verein. Limnol.*, 27, 311–315.
- Bangenal, T. B., & Tesch, F. W. (1978). Age and growth. In T. B. Bangenal (Ed.), *Methods for the assessment of fish production in fresh waters* (pp. 101–136). Oxford, UK: Blackwell.
- Degerman, E., Henrikson, L., Herrmann, J., & Nyberg, P. (1994). The effects of liming on aquatic fauna. In L. Henrikson & Y. W. Brodin (Eds.), *Liming of acidified surface waters a swedish synthesis*. Berlin Heidelberg New York: Springer.
- Dillon, P. J., Yan, N. D., Schneider, W. A., & Conroy, N. (1979). Acidic lakes in Ontario, Canada: Characterization, extend and responses to base and nutrient additions. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 13, 317–336.
- Eriksson, F., Hörnström, H., Mossberg, P., & Nyberg, P. (1983). Ecological effects of lime treatment of acidified lakes and rivers in Sweden. *Hydrobiologia*, 101, 145–164.
- Foote, K. G., Knudsen, H. P., Vestnes, G., MacLennan, D. N., & Simmonds, E. J. (1987). Calibration of acoustic instruments for fish density estimation. *ICES Cooperative Research Report*, 144, 1–70.
- Fott, J., Prazakova, M., Stuchlik, E., & Stuchlikova, Z. (1994). Acidification of lakes in Sumava (Bohemia) and in the High Tatras Mountains (Slovakia). *Hydrobiologia*, 274, 37–47.
- Freier, K., & Bollenbach, M. (2001). Auswirkung eines neuartigen Pufferungsverfahrens auf die Dominanzstruktur des phyto- und zooplanktons in einer versauerten Tal-sperre. *Deutsche Gesellschaft für Limnologie (DGL), Tagungsbericht*, 2000, 577–581.
- Gilbert, R. O. (1987). *Statistical methods for environmental pollution monitoring*. New York: Van Nostrand.
- Hirsch, R. M., & Slack, J. R. (1984). A nonparametric trend test for seasonal data with serial dependence. *Water Research Resources*, 20, 727–732.
- Hirsch, R. M., Slack, J. R., & Smith, R. A. (1982). Techniques of trend analyses for monthly water quality data. *Water Research Resources*, 18, 107–121.
- Hoehn, E., Clasen, J., Scharf, W., Ketelaars, H. A. M., Nienhüser, A. E., Horn, H., et al. (1998). *Erfassung und bewertung von planktonorganismen*. Oldenbourg Verlag, p. 151.
- Holt, C. A., & Yan, N. D. (2003). Recovery of crustacean zooplankton communities from acidification in Killarney Park, Ontario, 1971–2000: pH 6 as a recovery goal. *Ambio: A Journal of the Human Environment*, 32, 203–207.
- Hultberg, H., & Andersson, I. (1982). Liming of acidified lakes – induced long-term changes. *Water, Air and Soil Pollution*, 18, 333–342.
- Keitel, M. (1995). Langzeitbetrachtung der Gewässerversauerung – Fallstudie im Erzgebirge. *Wasser & Boden*, 47, 27–33.
- Keller, W., & Yan, N. D. (1998). Biological recovery from lake acidification: Zooplankton communities as a model of patterns and processes. *Restoration Ecology*, 6, 364–375.
- Keller, W., Yan, N. D., Somers, K. M., & Henneberry, J. H. (2002). Crustacean zooplankton communities in lakes recovering from acidification. *Canadian Journal of Fisheries and Aquatic Sciences*, 59, 726–735.
- Libiseller, C. (2002). MULTMK/PARTMK, a program for the computation of Multivariate and Partial Mann-Kendall Test. Retrieved from <http://www.mai.liu.se/~cllib/welcome/PMKtest.html>.
- McLennan, D. N., & Simmonds, E. J. (1992). *Fisheries acoustics*. London, UK: Chapman & Hall, p. 325.
- Niinioja, R., Ahtiainen, M., & Holopainen, A.-L. (1990). Liming of the acidified lake Valkealampi in eastern Finland: Effects on water chemistry and phytoplankton. In P. Kauppi, P. Anttila & K. Kentämies (Eds.), *Acidification in Finland* (pp. 1127–1143). Berlin Heidelberg New York: Springer.
- Nyberg, K., Vuorenmaa, J., Rask, M., Mannio, J., & Raitaniemi, J. (2001). Patterns in water quality and fish status of some acidified lakes in southern Finland during a decade: Recovery proceeding. *Water, Air and Soil Pollution*, 130, 1373–1378.
- Schaumburg, J. (2000). Long term trends in biology and chemistry of the acidified Bavarian Forest Lakes. *Silva Gabreta*, 4, 29–40.
- Schindler, D. W., Frost, T. M., Mills, K. H., Chang, P. S. S., Davies, I. J., Findlay, D. L., et al. (1991). Comparison between experimentally- and atmospherically-acidified lakes during stress and recovery. *Proceedings of the Royal Society of Edinburgh*, 97, 193–226.
- Tammi, J., Appelberg, M., Beier, U., Hesthagen, T., Lappalainen, A., & Rask, M. (2003). Fish status survey of nordic lakes: Effects of acidification, eutrophication and stocking activity on present fish species composition. *Ambio: A Journal of the Human Environment*, 32, 98–105.
- Tammi, J., Rask, M., Vuorenmaa, J., Lappalainen, A., & Vesala, S. (2004). Population responses of perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*) to recovery from acidification in small Finnish lakes. *Hydrobiologia*, 528, 107–122.

- Ulrich, K. U., Paul, L., & Meybohm, A. (2006). Response of drinking-water reservoir ecosystems to decreased acidic atmospheric deposition in SE Germany: Trends of chemical reversal. *Environmental Pollution*, 141, 42–53.
- Ulrich, K. U., Paul, L., Striebel, T., Dimitriadis, A., Knolle, M., & Belouschek, P. (2001). Water treatment in an acidified reservoir: Diacidification, buffering and precipitation of pollutants (in German with English abstract). *Vom Wasser*, 96, 159–172.
- Vrba, J., Kopacek, J., & Fott, J. (2000). Long-term limnological research of Bohemian Forest lakes and their recent status. *Silva Gabreta*, 4, 7–28.
- Vrba, J., Kopacek, J., Fott, J., Kohout, L., Nedbalova, L., Prazakova, M., et al. (2003). Long-term studies (1871–2000) on acidification and recovery of lakes in the Bohemian Forest (central Europe). *The Science of the Total Environment*, 310, 73–85.
- Willuweit, T., Weißgräber, S., Belouschek, P., & Lönz, P. (1995). A new method for successful water treatment (in German with English abstract). *Vom Wasser*, 85, 241–250.

Invasives, Introductions and Acidification: The Dynamics of a Stressed River Fish Community

Bjørn Mejdell Larsen · Odd Terje Sandlund ·
Hans Mack Berger · Trygve Hesthagen

Received: 16 June 2005 / Accepted: 23 June 2006 / Published online: 23 December 2006
© Springer Science + Business Media B.V. 2006

Abstract We describe the development of the fish community in the acidified and limed river Litleåna in southern Norway, and describe how chemical restoration, compensatory introductions of exotics, and accidental invasion of exotics interact to influence the population of the naturally occurring brown trout (*Salmo trutta*). The river Litleåna is a tributary to the river Kvina in Vest-Agder County, southern Norway. During the years 1996–2004, annual mean pH was 4.9–5.0 and 6.1–6.4 above and below the liming facility, which was installed in 1994. Originally, brown trout was the only fish species in the river, but brook trout (*Salvelinus fontinalis*) have been intentionally introduced, whereas European minnow (*Phoxinus phoxinus*) was introduced by accident. Fish densities were recorded by means of electrofishing annually over the ten year period 1995–2004. Although close to extinction before liming was initiated, brown trout fry densities increased from 1995 to 1999, with subsequent varying densities. There has

been a simultaneous major increase in the occurrence and density of European minnow since 1997. Our results show that both brown trout and European minnow increase after liming. Minnow densities are negatively affected by low pH episodes in the river. The growth rates of brown trout fry are negatively correlated to minnow densities, indicating competition between the species. Brook trout densities have decreased since liming started, and during the brown trout recovery.

Keywords brown trout · European minnow · brook trout · introduction · acidification · liming

1 Introduction

Pollution and introduced species are among the major threats to natural biodiversity. In southern Norway, acidification due to atmospheric deposition (acid rain) has caused local extinction of thousands of inland fish stocks. Simultaneously, intentional or unintentional introduction of non-native fish species has taken place in most water courses. Over the last decade, reduced levels of acidifying emissions and various mitigation measures, in particular liming of water courses, has improved living conditions for fish. The introduced species, however, are still there, and constitutes a major hindrance for a full restoration of the aquatic ecosystem.

B. M. Larsen (✉) · O. T. Sandlund · T. Hesthagen
Norwegian Institute for Nature Research,
Tungasletta 2,
7485 Trondheim, Norway
e-mail: bjorn.larsen@nina.no

H. M. Berger
Felt-BIO,
Flygata 6,
7500 Stjørdal, Norway

The development of a river fish community during chemical restoration after acidification has previously been documented (e.g. Larsen & Hesthagen, 2004). The impact of introduced fish species has also been described (e.g., Sandlund & Bongard, 2000; Museth, Borgstrom, Hame, & Holen, 2003). However, the development of a riverine fish community during chemical restoration, with the simultaneous complicating presence of non-native fish species has not been described.

This paper analyses the development of the fish community in the river Litlåna in southern Norway, and discusses how environmental conditions, compensatory introductions of exotics, and accidental invasion of exotics interact to influence the population of the naturally occurring brown trout (*Salmo trutta*).

2 Study Area

The river Litlåna is a tributary to the river Kvina in Vest-Agder County, southern Norway (Fig. 1). The calcium content in bedrock and sediments is low, and the capacity to buffer acidifying depositions is poor. Originally, brown trout was the only fish species in the river. Since 1980, when atmospheric pollution was about to wipe out the brown trout populations, the more low pH tolerant brook trout (*Salvelinus fontinalis*) have been introduced several times. Natural reproduction of brook trout has been recorded. European minnow (*Phoxinus phoxinus*) was detected in the river for the first time in 1997 (Berger, 1999), probably as a result of an accidental introduction in a tributary at least 10–12 years earlier (cf. Hesthagen & Sandlund, 1997).

2.1 Water Chemistry

To chemically restore the river, a liming facility was installed in 1994 (Fig. 1). Subsequently, water quality shows the typical trend of acidified rivers in this part of Norway, with mean pH at 4.9–5.0 above (station C5; Fig. 1) and 6.1–6.4 below (station C8; Fig. 1) the liming facility (Fig. 2; Kaste & Skancke, 2004; personal communication). Although pH around 6 normally is adequate for brown trout and other sensitive fish species, the observed drops in pH values to below 5.5 (Fig. 2) indicates a precarious

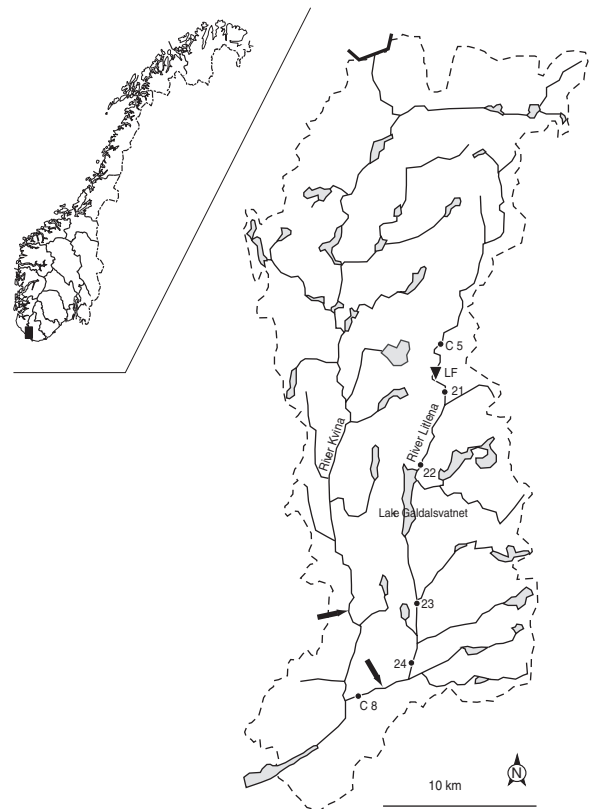


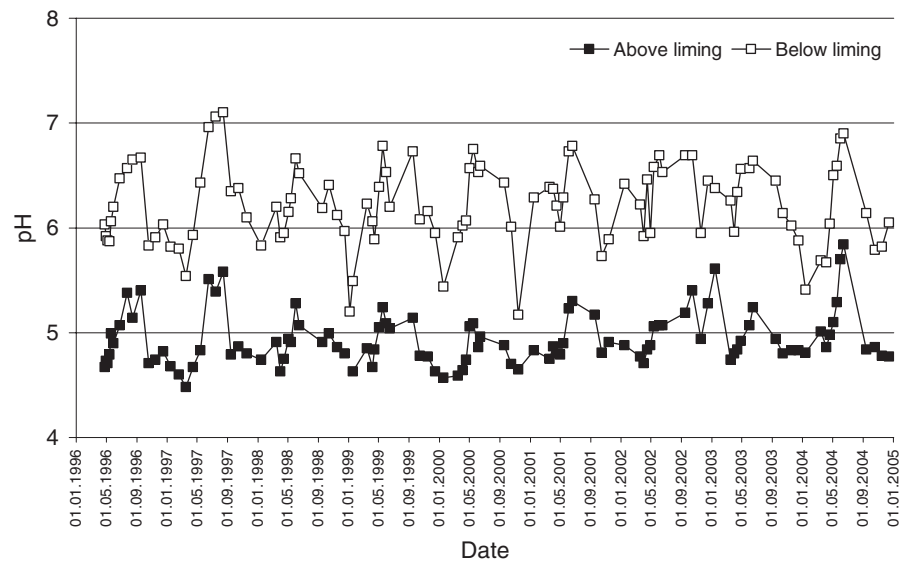
Fig. 1 Location of the study area in River Litlåna with electrofishing localities (21–24), the liming facility (LF), and localities for chemical analysis (C5–C8). The arrows indicate the upper part of the river sections with anadromous salmonids

environment for some fish species. These drops in pH are usually associated with high precipitation, followed by high water flows in the river. Calcium levels in Litlåna above the liming facility has over the years 1996–2004 only occasionally been above 0.5 mg Ca l^{-1} . Below the liming facility, calcium levels are normally around 2 mg Ca l^{-1} , but with occasional drops to just above 1 mg Ca l^{-1} (Kaste & Skancke, 2004; personal communications).

3 Sampling Methods

Sampling was performed annually with a portable back-pack electric fishing apparatus at four localities below the liming facility. Fishing was performed in August every year over the 10-year period 1995–2004. Each locality was fished three times (removal method; Bohlin, Hamrin, Heggberget, Rasmussen, &

Fig. 2 pH above and below the liming facility in Litlåna, from January 1996 to January 2005



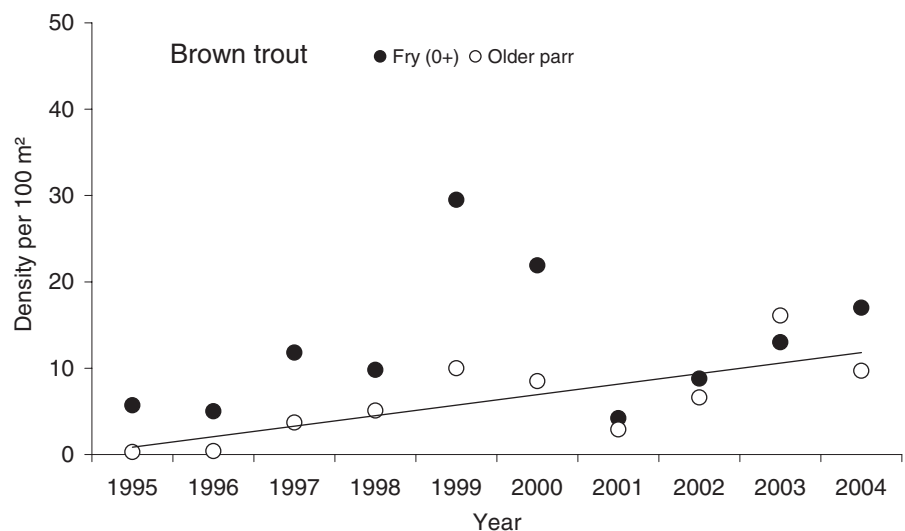
Salveit, 1989; Zippin, 1958), and all fish was identified to species. All body lengths were measured in the field.

4 Results

Brown trout was close to extinction and very few anglers took an interest in fishing in Litlåna before liming was initiated (Kvinesdal kommune, 1999). During the first two years of sampling (1995–96), the total density of brown trout fry (0+) and older parr was at only 6 and 5 fish 100 m⁻², respectively (Fig. 3). Subsequently, brown trout densities in-

creased to a maximum of 40 fish 100 m⁻² in 1999. The dramatic increase was mainly caused by fry, which reached a density of 30 fish 100 m⁻² that year. The density of older parr showed a more steady increase up to 1999. In 2001, however, brown trout density decreased dramatically to only 7 fish 100 m⁻². Again, the density differences were more dramatic for fry (0+) than for older fish. Since 2001 brown trout densities have increased steadily to nearly 30 fish 100 m⁻². The overall tendency for brown trout over the period 1995–2004 is a significant density increase only for older parr ($\geq 1+$) ($F_{1,8}=10.36$; $r^2=0.56$; $P<0.05$) (Fig. 3). Brown trout densities vary in a similar pattern at the four sampling stations.

Fig. 3 Densities of brown trout fry (0+) (ns) and older parr ($\geq 1+$) ($F_{1,8}=10.36$; $r^2=0.56$; $P<0.05$) in Litlåna, 1995–2004. The sampling localities 21–24 were pooled. Fitted regression line is indicated



Brook trout was first introduced to several small lakes in Litlåna in the beginning of the 1980s (Berger, 1999), and later spread to the main stem of Litlåna. The purpose of this introduction was to compensate for the loss of acid-sensitive brown trout by establishing a population of the acid-tolerant brook trout. When the monitoring programme started in 1995, the mean total density of brook trout was 9 fish 100 m⁻², and the population density reached a maximum in 1998, at 11 fish 100 m⁻² (Fig. 4). Brook trout has mainly been found at the three upper sampling stations, in particular at the station upstream of Lake Galdalsvatn. Spawning has also been observed at this locality. At the river stations, more than 90% of the brook trout was fry (0+) during these years, indicating a solid recruitment level. There is a significant decrease in the number of brook trout fry over the ten year period 1995–2004 ($F_{1,8}=18.26$; $r^2=0.70$; $P<0.005$) (Fig. 4), and densities of brook trout have steadily decreased to less than 0.6 fish 100 m⁻², i.e. the species is now nearly extinct in the river.

European minnow has most likely been introduced to a tributary to Litlåna in the 1980s. In the main stem of Litlåna, our electrofishing surveys first detected the species at the upstream sampling station in 1997, in low densities (0.6 fish 100 m⁻²) (locality 21; Fig. 5). A swift population increase over the following three years brought the minnow density at this sampling locality to a maximum of 162 fish 100 m⁻² in 2000. A temporary decrease in 2001 was followed by a further increase up to 537 fish 100 m⁻² in 2003. During the years since the establishment of

minnow at the upper sampling locality (by 1999), densities of minnow has been 12–75 times higher than age-0 brown trout at this locality. Downstream migration of minnow has occurred in conjunction with the population expansion at the upper locality. Minnows were detected at locality 22, which is 6.5 km downstream from locality 21, in 2002. The initial density at this locality was 11 fish 100 m⁻², but already one year later densities were above 200 fish 100 m⁻². In 2004, the first minnows were recorded at locality 24, which is 8 km below the outlet of the 4.5 km long lake Galdalsvatn. This indicates a downstream migration rate of 19.0 km over seven years, i.e. approximately 2.7 km year⁻¹. The first individuals of minnow to be caught at any locality were always large and adult fish. Thus, the adult minnows (60–80 mm in length) are the pioneers of downstream migration, and become the first colonizers of new habitats in the river. In the established minnow populations, recruitment is variable among years. The proportion of fish <40 mm (age $\leq 2+$) was 42–44% in 1998 and 2003. In 2001 and 2002 no small minnows were recorded, while the proportion in the remaining years was 2–5%.

The length distribution of brown trout fry is nearly identical to minnows older than two years (Fig. 6). There was a significant reduction in trout fry lengths during 1995–2004 ($F_{1,8}=15.56$; $r^2=0.62$; $P<0.005$). There was a non-significant decrease with brown trout density ($P=0.12$), but a significant decrease in trout fry lengths with increasing minnow density ($F_{1,8}=8.44$; $r^2=0.45$; $P<0.05$) (Fig. 7).

Fig. 4 Densities of brook trout fry (0+) ($F_{1,8}=18.26$; $r^2=0.70$; $P<0.005$) and older parr ($\geq 1+$) (ns) in Litlåna, 1995–2004. The sampling localities 21–24 were pooled. Fitted regression line is indicated

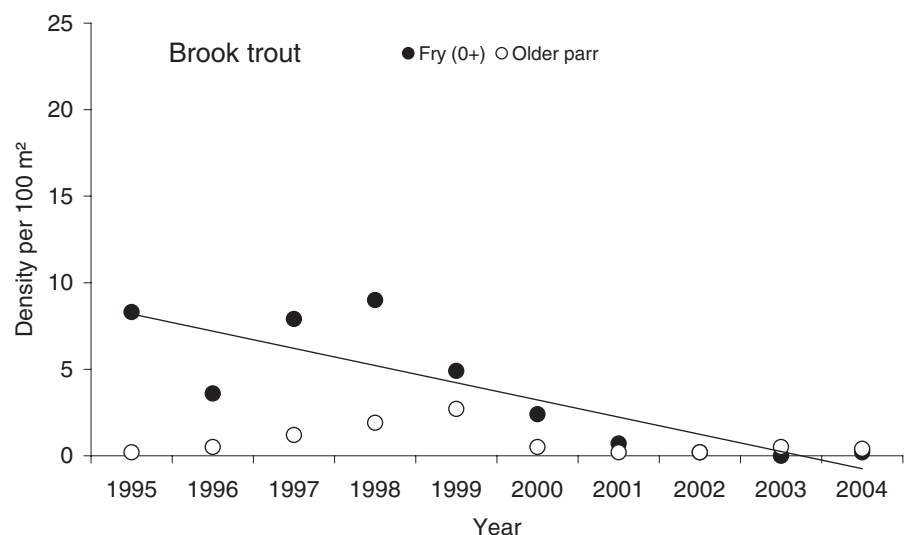
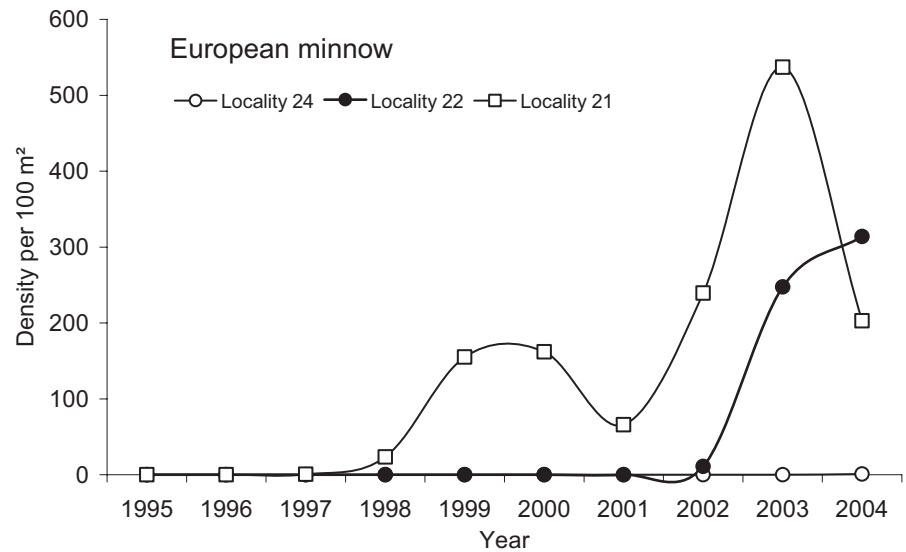


Fig. 5 Densities of European minnow in Litlåna, localities 21, 22 and 24 during 1995–2004



We may assume that minnow became well established at locality 21 since 1999, and at locality 22 since 2003 (Fig. 5). During the post-establishment years, our data indicate that minnow densities increase with increasing minimum pH-values (recorded during the preceding 10 months) up to approximately 5.7 (Fig. 8). At higher pH values, minnow densities appear not to be affected. This suggests that episodes with low pH values cause some mortality in the minnow population.

The densities of brown trout and brook trout were not significantly related to water pH, nor was there any significant correlation between minnow densities

and the total densities of brown trout and brook trout, respectively.

5 Discussion

Our results from River Litlåna demonstrate that chemical restoration of acidified rivers by liming favours brown trout over the intentionally introduced brook trout, while liming also benefits the accidentally introduced European minnow.

It appears that minnow is very sensitive to water quality, and that densities decrease whenever there is

Fig. 6 Length distribution of brown trout, brook trout and European minnow sampled in Litlåna during 1995–2004

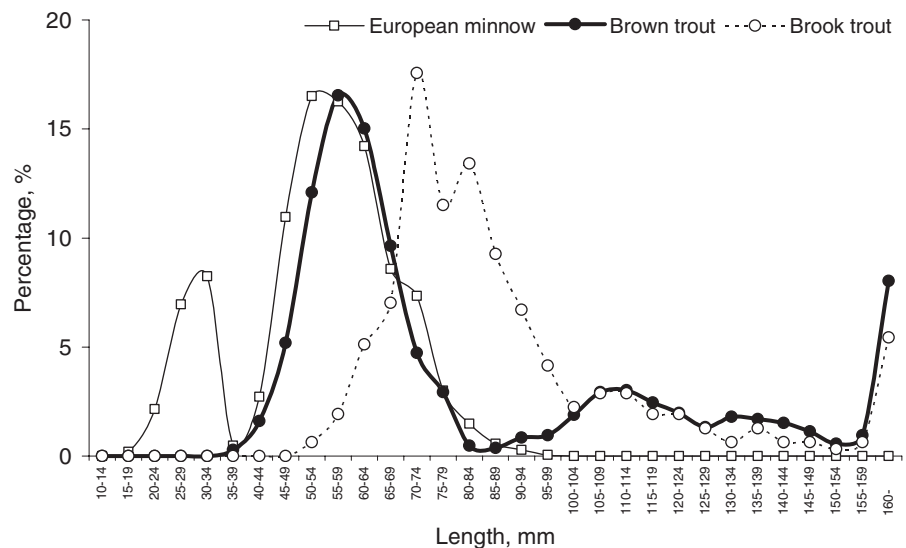
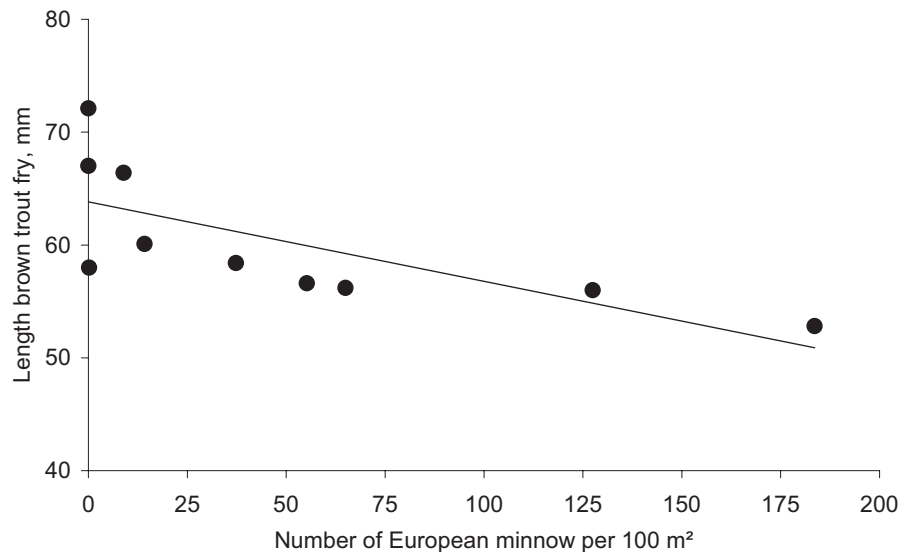


Fig. 7 The relation between densities of European minnow and the body length of brown trout fry (0+) in Litlåna, 1995–2004 ($F_{1,8}=8.44$; $r^2=0.45$; $P<0.05$). Fitted regression line is indicated



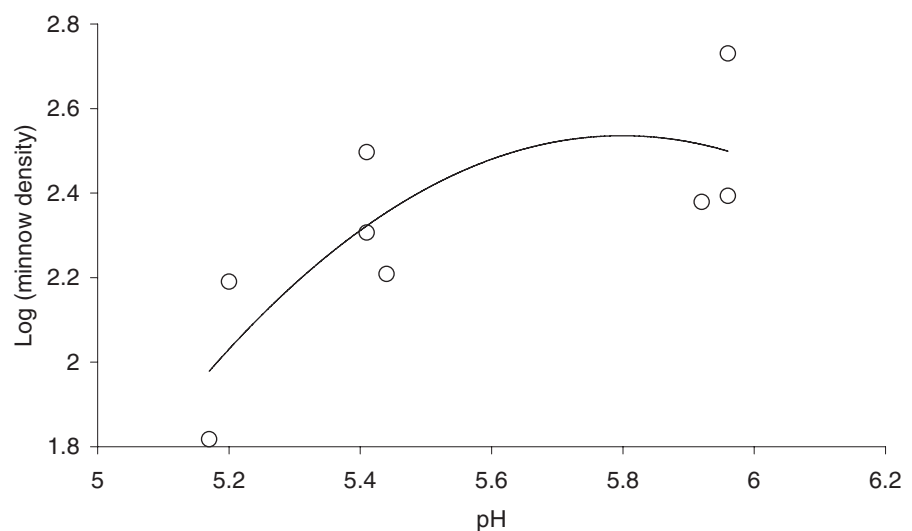
any low-pH episode in the river. Neither brown trout nor brook trout appear to be that clearly influenced by pH in the post liming period. However, the number of sampling years may be too low to demonstrate any correlation in this regard.

We would have expected brown trout fry densities to be negatively correlated to minnow densities. This is not the case, but possible impacts of minnow on brown trout are indicated by the decreasing growth of brown trout fry with increasing minnow densities. The mechanism behind this impact in streams may be assumed to be competition for the same food sources (Hesthagen, Hegge, & Skurdal, 1992). The fact that brown trout fry and the major part of the 2+ and older

minnows overlap almost completely in length supports the notion that the two species may compete for food in relatively small streams where habitat overlap between the two species may be significant.

The brook trout has been introduced in many Scandinavian water courses, both in good quality waters and in rivers subjected to acidification. The intention has been to establish the species as a target for anglers, either in addition to the native brown trout, or to replace the locally extinct brown trout populations. This obviously complicates the process to restore native fish communities through chemical restoration of water quality. However, the development in Litlåna seems to support the assumption that brook trout loses

Fig. 8 Minnow density in August at locality 21 (1998–2004) and locality 22 (2003–2004) as a function of the minimum pH recorded the preceding 10 months ($F_{2,5}=4.07$; $r^2=0.62$; $P=0.09$). The selected years are subsequent to the “boom” phase years in population establishment. Fitted regression line is indicated



out in competition with brown trout under reasonable water quality conditions. In Scandinavian streams, it is commonly observed that brook trout is restricted to the uppermost source sections when coexisting with brown trout (Grande, 1982; Nyman, 1970).

European minnow is swiftly becoming the most common fish species in Norwegian inland waters (Hesthagen & Sandlund, 1997; Taugbøl, Hesthagen, Museth, Dervo, & Andersen, 2002). Introductions occur through accidental releases by careless anglers, transfer of water among water bodies through hydropower or water supply tunnels, etc. (Sandlund & Bongard, 2000). Because the species is very sensitive to low pH, it will not establish strong populations in acid waters (Almer, 1972; Hultberg, 1977). Our data also indicates that minnow survival is sensitive to acid episodes. However, chemical restoration of acid waters will favour the minnow, and when the species live in sympatry, the intended restoration of brown trout populations may face somewhat unexpected problems. Minnow has a two-tiered role in relation to brown trout. Brown trout fry and minnow may compete for food when they share habitats, which may most often occur in the nursery streams of brown trout. Larger brown trout, however, may prey on minnows, and thereby increase their growth rates, if their habitats overlap (Museth et al., 2003; Taugbøl et al., 2002). In Litlåna, brown trout may very rarely reach a body size which enables it to prey on minnows.

In summary, both brown trout and minnows are favoured by liming in acidified rivers and streams. Minnow densities have a negative impact on the growth rates of brown trout fry, and may therefore cause brown trout restoration not to fully reach its potential. Brook trout densities decrease as pH values are brought back to around 6, allowing brown trout and minnow densities to increase. However, there was no significant correlation between minnow densities and the densities of brown trout and brook trout, respectively over our 10 years of sampling.

References

- Almer, B. (1972). Förurningens inverkan på fiskbestånd i västkustsjöar (The impact of acidification on the fish stocks in Swedish west coast lakes). *Information från Sötvattenlaboratoriet, Drottningholm* 12–1972, 47 pp. (In Swedish).
- Berger, H. M. (1999). Ørekyte (*Phoxinus phoxinus*) i Litleåna I Kvinavassdraget i Vest-Agder 1998 (Distribution of European minnow (*Phoxinus phoxinus*) in the River Litleåna (Kvina watershed) in the County of Vest-Agder, Southern Norway). *NINA Oppdragsmelding* 580, 29 pp. (In Norwegian with English summary).
- Bohlin, T., Hamrin, S., Heggberget, T. G., Rasmussen, G., & Saltveit, S. J. (1989). Electrofishing-theory and practice with special emphasis on salmonids. *Hydrobiologia*, 173, 9–43.
- Grande, M. (1982). Introduction and the present status of brook charr (*Salvelinus fontinalis* Mitchell) in Norway, EIFAC Symposium “Stock enhancement in the management of freshwater fisheries”. Budapest.
- Hesthagen, T., Hegge, O., & Skurdal, J. (1992). Food choice and vertical distribution of European minnow, *Phoxinus phoxinus*, and young native and stocked brown trout, *Salmo trutta*, in the littoral zone of a subalpine lake. *Nordic Journal of Freshwater Research*, 67, 72–76.
- Hesthagen, T., & Sandlund, O. T. (1997). Endringer i utbredelse av ørekyte i Norge: årsaker og effekter (Changes in the distribution of European minnow, *Phoxinus phoxinus*, in Norway: causes and effects). *NINA Fagrapport* 13, 16 pp. (In Norwegian with English summary).
- Hultberg, H. (1977). Thermally stratified acid water in late winter – a key factor inducing self-accelerating processes which increase acidification. *Water, Air and Soil Pollution*, 7, 279–294.
- Kaste, Ø., & Skancke, L. B. (2004). Kvinavassdraget. 2. Vannkjemi i direktoratet for naturforvaltning. *Kalking i vann og vassdrag. Effektkontroll av større prosjekter 2003*, DN-Notat 2004-2, pp. 103–104. (In Norwegian).
- Kvinesdal kommune (1999). Vassdragsplan for Kvinavassdraget. *Kvinesdal kommune*, Report, no pagination. (In Norwegian).
- Larsen, B. M., & Hesthagen, T. (2004). Laks i kalkede vassdrag i Norge. Status og forventninger (Atlantic salmon in limed Norwegian rivers. Present status and expectations). *NINA Fagrapport* 81, 25 pp. (In Norwegian with English summary).
- Museth, J., Borgstrøm, R., Hame, T., & Holen, L. A. (2003). Predation by brown trout: a major mortality factor for sexually mature European minnows. *Journal of Fish Biology*, 62, 692–705.
- Nyman, O. L. (1970). Ecological interactions of brown trout, *Salmo trutta* L., and brook trout, *Salvelinus fontinalis* (Mitchill) in a stream. *Canadian Field Naturalist*, 84, 343–350.
- Sandlund, O. T., & Bongard, T. (2000). The freshwater environment. In: I. R. Weidema (Ed.), *Introduced species in the Nordic countries*. Nordisk ministerråd, København, NORD 2000, 13, 87–122.
- Taugbøl, T., Hesthagen, T., Museth, J., Dervo, B., & Andersen, O. (2002). Effekter av ørekyteintroduksjoner og utfiskingstiltak-en vurdering av kunnskapsgrunnlaget (Effects of European minnow introductions and fish removal actions-an evaluation of existing knowledge). *NINA Oppdragsmelding* 753, 31 pp. (In Norwegian with English summary).
- Zippin, C. (1958). The removal method of population estimation. *Journal of Wildlife Management*, 22, 82–90.

Fish Stomachs as a Biomonitoring Tool in Studies of Invertebrate Recovery

Arne Fjellheim · Åsmund Tysse · Vilhelm Bjerknes

Received: 12 June 2005 / Accepted: 24 June 2006 / Published online: 12 January 2007
© Springer Science + Business Media B.V. 2007

Abstract High mortality rates due to predation from fish may reduce densities of preferred prey animals. Predation may also depress the rate of recovery from environmental stress. In an alpine ecosystem damaged by acidification, we compared three different techniques of monitoring the recovery of two large species of crustaceans, the amphipod *Gammarus lacustris* and the notostrachan *Lepidurus arcticus*. The methods used were: (1): benthic littoral kick samples, (2): artificial substrate in the form of jute bags, (3): examination of brown trout stomachs. The monitoring took place in two limed lakes at the Hardangervidda mountain plateau in Central Norway, L. Svartavatn and L. Svartavasstjørni. Brown trout, *Salmo trutta*, is the only fish species in the lakes. Liming as a water quality improvement measure was

started in 1994. All stomach samples were negative with respect to *Gammarus* and *Lepidurus* during the period 1987–1998. In 1999, the first records of both species were done in trout stomachs collected from Lake Svartavatnet. In Lake Svartavasstjørni, *Lepidurus* and *Gammarus* reappeared in fish stomachs in 2001 and 2002, respectively. During the period of monitoring, no records of these crustaceans were done in benthic samples and on artificial substrate in any of the two lakes. In an unacidified reference site, Lake Skiftesjøen, both benthic samples and the jute bags indicated a dense population of *Gammarus*. Our results strongly indicate that studies of fish stomachs are the best method for monitoring low-density populations of attractive fish food animals.

Keywords liming · mountain lakes · *Lepidurus* · *Gammarus* · brown trout stomachs

A. Fjellheim (✉)
Department of Biology,
University of Bergen,
LFI, Thor Møhlensgt. 49,
5006 Bergen, Norway
e-mail: arne.fjellheim@bio.uib.no

Å. Tysse
Department of Environment,
Box 1604, 3007 Drammen, Norway

V. Bjerknes
Norwegian Institute for Water Research,
Nordnesboder 5,
5005 Bergen, Norway

1 Introduction

The energetic cost of food intake and the quality of the food are important factors for most living animals. Brown trout (*Salmo trutta* L.) may normally chose between a wide range of food items including both animals produced in fresh water and animals of terrestrial origin. In Norway, both the amphipod *Gammarus lacustris* G. O. Sars and the notostrachan *Lepidurus arcticus* Pallas is considered to be some of

the most important food items for brown trout populations in the Norwegian mountain areas (Borgstrøm & Hendrey, 1976; K. A. Økland & J. Økland, 1985; Sømme, 1934). The two species accounted for 25% (*Gammarus*) and 15% (*Lepidurus*) of the yearly energy budget of brown trout in Lake Øvre Heimdalsvatnet (1,090 m o.h.) during 1969–1972 (Lien, 1978). Both species are highly vulnerable to acidification. Borgstrøm and Hendrey, (1976) demonstrated experimentally that the first larval stages of *L. arcticus* and adult *G. lacustris* was negatively effected at pH lower than 5.5, a condition which in poorly buffered areas may occur during snowmelt. In Norway, *G. lacustris* is absent from lakes with pH values below 6.0 (Økland, 1980), while *L. arcticus* has not been recorded in lakes with pH below 6.1 (Borgstrøm, Brittain, & Lillehammer, 1976).

The diet of brown trout normally reflects a strong selection process. The strength of the selection is affected by several factors, of which prey density, prey size, quality, catchability and learning (Allen, 1988; Dahl, 1998; Reiriz, Nicieza, & Brana, 1998; Salvanes & Hart, 1998; Sweka & Hartman, 2001; Warburton, 2003) are the most important. As a consequence of this, large nutrient-rich food items may be strongly selected (Dahl, 1915; Dedual, Maxwell, Hayes, & Strickland, 2000). A secondary effect of this may be strongly reduced prey densities (McNaught et al., 1999; Pechlaner, 1984). Attractive prey animals may be difficult to detect using conventional benthic sampling due to low density and/or patchy distribution (Borgstrøm, 1970). In many cases, records of large crustaceans are solely based on observations from fish stomachs (Aass, 1969; Berg, 1954; Hesthagen, 1979; Runnström & Määr, 1950; Sømme, 1934).

This paper deals with the monitoring of the food of a rare and endangered trout variety, the fine-spotted brown trout (Skaala & Jørstad, 1987). The populations are located in three lakes, L. Svartavasstjøni (1,243 m a.s.l.), L. Svartavatnet (1,233 m a.s.l.) and L. Dragøyfjorden (1,180 m a.s.l.), at the Hardangervidda mountain plateau (Fig. 1). The trout suffered severe recruitment failure due to acidification around 1987. Several actions were initiated to restore the trout and its natural environment (Fjellheim, Tysse, & Bjerknes, 2001). Amongst these were a liming program, starting in 1994 and stocking of *G. lacustris*

and *L. arcticus* (1997–2000). The former was reported to be the most important trout food in the period 1970–1987, prior to the acidification damages (Madsen, 1986). A programme aiming to monitor eventual effects of the stocking of the food animals was initiated in 1997. We used three different methods of sampling: (1) benthic littoral kick samples, (2) artificial substrate in the form of jute bags and (3) examination of fish stomachs. Our hypothesis was that (1) Examination of fish stomachs is the best method of detecting low-density/patchy distributed populations of these animals due to food selection and (2) The populations of both *G. lacustris* and *L. arcticus* should benefit from the improved water quality and build up populations strong enough to constitute a major trout food source.

2 Materials and Methods

The study area is situated in the upper part of River Numedalslågen, South Norway. Two limed lakes, L. Svartavatnet (1,233 m a.s.l., 113 ha) and L. Svartavasstjøni (1,243 m a.s.l., 39.4 ha) were sampled. Reference samples were taken from an unlimed lake, L. Skiftesjøen (1,239 m a.s.l.) in a branch of the same watershed, app. 15 km in distance from the main lakes (Fig. 1). The reference lake, which is unacidified, was earlier used for collecting *Gammarus* and *Lepidurus* for stocking.



Fig. 1 Map showing the situation of Lake Svartavasstjøni, Lake Svartavatnet and the reference site Lake Skiftesjøen

Water samples were taken 5–11 times each year, at regular intervals during the ice-free season. Benthic invertebrates were monitored using three different techniques. Qualitative kick samples of benthic invertebrates were taken from the littoral zone using a sweep-net with mesh size 250 μm . One locality in L. Skiftesjøen and three different localities L. Svartavatnet and L. Svartavasstjørni were sampled. One sample was taken at each locality. Total kicking time was approximately 2 min and included different substrates. The substrate in the lakes consisted of stones, gravel and sand with no macrovegetation. The sampling took place in August/September each year. In July 2000, bags of jute (Dahl, 1915) were placed in the lakes at three different localities in each limed lake (three bags in each locality) and one locality in the reference lake (four bags). The jute bags were emptied for the first time in September 2000 and after that once a year until 2003, when the

bags had started disintegrating and the experiment was terminated.

Brown trout stomach samples were collected during 1997–2004. Additionally, we used earlier observations from test fishing in the period prior to 1997 (Elnan, 1991; Madsen, 1975, 1986, 1988). Test-fishing was performed in August/September each year using a standard series of bottom gillnets (Jensen, 1977), identical to earlier catch methods (Madsen, 1975, 1986, 1988). All brown trout size-classes present in the lake were represented in the samples due to the different selectivity of the gillnets. Due to an initially weak trout population, L. Svartavasstjørni was not test-fished in 1997 and 1999. The whole stomach content of each fish was studied as a single unit, except for a few samples in L. Svartavatnet in 1999 and 2000, which were pooled. All samples were preserved in ethanol and later sorted and identified at the laboratory, using a binocular. The vol.% composition of food

Table 1 Mean pH, conductivity (25°C), calcium, total aluminium and inorganic labile aluminium in the outlets of L. Svartavasstjørni and L. Svartavatnet in 1993 (before liming) and during 1994–2004 (limed)

	N samples	pH	Cond $\mu\text{S cm}^{-1}$	Ca mg l^{-1}	Alr $\mu\text{g l}^{-1}$	Ali $\mu\text{g l}^{-1}$
L. Svartavasstjørni outlet						
1993	6	5.46 (5.17–5.74)	12.7 (5.4–20.0)	0.50 (0.28–0.84)	68.2 (50–112)	37.8 (21–58)
1994	6	5.77 (5.54–5.91)	4.6 (4.5–4.7)	0.50 (0.48–0.53)	8.2 (4–12)	4.2 (2–6)
1995	11	6.25 (5.58–6.80)	8.8 (4.8–14.1)	0.93 (0.40–1.53)	12.6 (3–23)	2.5 (0–11)
1996	11	6.32 (6.03–6.63)	8.9 (6.8–12.9)	0.99 (0.69–1.52)	17.9 (13–25)	2.4 (0–5)
1997	11	6.54 (5.97–7.07)	10.5 (6.4–15.3)	1.34 (0.59–1.95)	19.5 (13–27)	3.5 (2–5)
1998	11	6.41 (6.07–6.65)	8.2 (5.7–15.0)	0.96 (0.54–2.04)	19.3 (13–35)	2.3 (0–5)
1999	11	6.62 (6.10–7.27)	10.4 (6.4–15.1)	1.42 (0.57–2.40)	22.4 (8–31)	2.3 (0–4)
2000	11	6.55 (6.06–7.12)	10.4 (5.9–16.5)	1.29 (0.65–2.44)	18.6 (9.0–36.5)	2.5 (1–6)
2001	8	6.55 (6.30–6.90)	9.6 (6.1–13.8)	1.36 (0.81–2.00)	20.4 (9.3–29.2)	2.5 (0–7)
2002	7	6.64 (6.14–7.11)	10.5 (6.8–16.7)	1.33 (0.71–2.54)	18.2 (11.6–29.1)	2.1 (0–8)
2003	8	6.69 (6.10–7.01)	14.3 (8.7–20.1)	1.94 (0.59–3.25)	19.2 (9.9–27.3)	1.5 (0–3)
2004	8	6.62 (6.27–6.94)	11.0 (7.5–17.7)	1.42 (0.88–2.47)	17.4 (10.5–20.8)	1.1 (0–5)
L. Svartavatnet outlet						
1993	5	5.45 (5.18–5.69)	11.3 (6.8–18.6)	0.5 (0.35–0.77)	58.8 (46–74)	31.2 (17–45)
1994	6	5.98 (5.84–6.12)	5.0 (4.8–5.3)	0.32 (0.30–0.36)	4 (0–7)	2.3 (0–4)
1995	11	6.02 (5.69–6.31)	6.5 (5.2–9.8)	0.51 (0.43–0.60)	9.9 (3–20)	1.8 (0–7)
1996	11	6.24 (6.01–6.36)	7.5 (6.5–9.9)	0.75 (0.67–1.03)	13.9 (9–20)	1.8 (0–5)
1997	11	6.36 (5.86–6.70)	8.4 (6.9–9.9)	0.92 (0.70–1.16)	15.5 (11–26)	1.7 (0–3)
1998	11	6.49 (6.10–6.64)	8.5 (6.7–12.3)	1.02 (0.75–1.62)	18.1 (11–32)	2.5 (1–6)
1999	11	6.59 (6.26–6.82)	8.9 (6.9–12.3)	1.16 (0.87–1.71)	17.5 (9–28)	2.1 (0–4)
2000	11	6.53 (6.28–6.74)	9.3 (6.8–12.7)	1.12 (0.81–1.60)	13.3 (3.0–21.9)	1.6 (0–4)
2001	8	6.58 (6.43–6.70)	9.1 (7.4–12.8)	1.22 (0.96–1.50)	17.1 (10.4–25.5)	2 (0–5)
2002	8	6.58 (6.31–6.89)	8.7 (5.8–12.0)	1.07 (0.65–1.60)	14.6 (8.7–18.1)	1.4 (0–4)
2003	8	6.62 (6.28–6.77)	11.0 (9.0–14.9)	1.42 (0.92–1.91)	13.9 (8.5–21.0)	0.5 (0–2)
2004	8	6.63 (6.30–6.85)	10.6 (9.1–13.3)	1.33 (1.09–1.78)	13.0 (6.8–25.2)	0.9 (0–2)

Minimum and maximum values are shown in parenthesis.

items in the stomach samples were estimated according to the “point’s method” of Hynes (1950).

3 Results

The results from the water samples reflect the oligotrophic nature of the lakes. Mean conductivity was lower than $15 \mu\text{S cm}^{-1}$ in both lakes. In 1993, before liming, minimum pH was 5.17 and 5.18 in the outlet of the two localities (Table 1). Calcium was low

and the inorganic labile aluminium was high, maximum $112 \mu\text{g l}^{-1}$ in the outlet of L. Svartavasstjørni. After liming pH increased markedly, and has stabilised around 6.5 during the later years. At the same time, mean values of labile aluminium was reduced to values below $5 \mu\text{g l}^{-1}$.

The diet of brown trout in both lakes was dominated by Cladocera, Trichoptera, Chironomidae and other dipterans (Table 2). *G. lacustris* and *L. arcticus* were absent in L. Svartavatnet until 1999, when the first records after liming was made. During

Table 2 Volume % stomach content (standard deviation) of brown trout from test fishing in L. Svartavatnet and L. Svartavasstjørni during 1997–2004

L. Svartavatnet	1997	1998	1999 ^a	2000 ^a	2001	2002	2003	2004
Stomachs examined	11	10	43	38	50	81	51	47
<i>Gammarus lacustris</i>	0.0	0.0	3.7	2.5	2.1 (7.0)	4.0 (15.0)	2.4 (12.2)	0.2 (1.5)
<i>Lepidurus arcticus</i>	0.0	0.0	5.9	17.6	5.0 (15.8)	14.0 (30.8)	0.2 (1.1)	0.4 (2.3)
Cladocera	39.8 (42.1)	40.8 (41.9)	19.1	55.9	76.5 (32.9)	51.2 (40.9)	81.2 (31.4)	62.3 (41.2)
Gastropoda	0.0	0.0	0.7	0.0	0.0	0.0	0.3 (2.1)	0.2 (1.6)
Oligochaeta	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
Bivalvia	0.0	0.0	0.0	0.0	0.1 (0.9)	0.0	0.0	0.0
Plecoptera l.	0.0	0.0	0.0	0.1	0.0	0.1 (0.8)	0.1 (0.5)	1.0 (5.9)
Trichoptera	54.9 (38.4)	37.3 (47.0)	11.8	1.8	6.6 (14.8)	3.8 (14.4)	6.7 (17.5)	9.6 (19.6)
Chironomidae	0.0	11.5 (29.0)	3.3	20.6	2.1 (11.4)	3.1 (8.9)	2.0 (6.1)	0.5 (1.0)
Other Diptera	0.5 (1.2)	3.5 (7.8)	52.0	0.0	3.6 (16.6)	0.2 (1.0)	2.1 (13.0)	1.5 (9.4)
Megaloptera	0.0	0.0	0.9	0.1	0.1 (0.6)	23.4 (33.5)	1.7 (10.4)	9.5 (26.0)
Corixidae	0.0	0.0	0.0	0.0	0.0	0.1 (0.8)	0.0	0.0
Coleoptera aq.	1.7 (5.5)	6.8 (19.6)	0.9	1.1	4.0 (12.3)	0.0	2.5 (9.3)	2.4 (6.5)
Div Terr	3.1 (10.3)	0.0	1.4	0.3	0.0	0.1 (0.3)	0.7 (3.3)	10.9 (24.9)
Mammals	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6 (11.0)
L. Svartavasstjørni	1997	1998	1999	2000	2001	2002	2003	2004
Stomachs examined	0	23	0	49	33	46	57	49
<i>Gammarus lacustris</i>		0.0		0.1 (0.4)	0.0	1.7 (8.0)	1.6 (11.8)	0.0
<i>Lepidurus arcticus</i>		0.0		0.0	1.5 (6.0)	22.4 (35.2)	1.5 (11.0)	0.8 (5.3)
Cladocera		60.2 (37.7)		1.9 (4.5)	13.5 (29.7)	26.9 (37.1)	36.5 (40.9)	39.3 (39.6)
Gastropoda		0.0		0.0	1.7 (9.9)	0.0	0.0	2.1 (14.3)
Bivalvia		0.0		0.0	1.1 (4.4)	0.0	0.4 (2.1)	2.0 (14.3)
Ephemeroptera		0.0		0.0	0.0	0.0	0.0	4.6 (16.9)
Plecoptera l.		0.0		0.2 (1.6)	0.0	0.1 (1.5)	0.0	0.8 (2.9)
Trichoptera		19.2 (31.2)		2.5 (6.6)	7.9 (20.5)	4.4 (15.5)	14.5 (27.9)	29.6 (38.1)
Chironomidae		20.3 (28.0)		93.1 (12.1)	2.2 (6.1)	2.3 (8.5)	2.2 (8.2)	2.9 (5.0)
Other Diptera		0.0		0.0	26.5 (31.6)	34.8 (38.5)	28.7 (35.8)	1.8 (6.3)
Megaloptera		0.0		0.0	0.0	0.0	0.3 (2.0)	0.0
Coleoptera aq.		0.0		0.4 (1.8)	26.2 (26.6)	4.3 (17.3)	3.1 (13.3)	2.8 (14.7)
Div Terr		0.2 (1.2)		1.7 (4.8)	16.3 (18.3)	3.2 (6.1)	11.3 (24.9)	9.7 (24.0)
Mammals		0.0		0.0	0.0	0.0	0.0	3.6 (17.8)
Brown trout		0.0		0.0	3.0 (17.1)	0.0	0.0	0.0

All fish caught in August/September.

^a: Standard deviation not calculated due to pooling of some of the samples

Table 3 Mean % distribution of animals (range) per sample of benthos and jute bags in L. Svartavatnet, L. Svartavasstjørni and the reference L. Skiftesjøen

Taxon	Lake Svartavatnet		Lake Svartavasstjørni		Lake Skiftesjøen	
	Benthic samples	Jute bags	Benthic samples	Jute bags	Benthic samples	Jute bags
<i>Gammarus lacustris</i>	0.0	0.0	0.0	0.0	6.4 (2.7–10.2)	28.4 (12.4–57.1)
<i>Lepidurus arcticus</i>	0.0	0.0	0.0	0.0	1.8 (0–8.5)	0.0
Cladocera	11.1 (4.2–21.8)	43.5 (32.2–53.3)	12.8 (5.5–27.5)	10.3 (5.7–14.1)	14.8 (2.4–63.7)	17.1 (8.9–21.7)
Copepoda	12.4 (3.6–18.0)	8.0 (5.8–12.5)	12.1 (5.1–17.3)	5.9 (3.8–9.0)	2.8 (0–8.7)	4.4 (1.4–8.5)
Ostracoda	0.8 (0–3.1)	0.5 (0–0.8)	0.4 (0–0.9)	0.4 (0–1.2)	1.2 (0.2–2.3)	1.6 (0.2–4.5)
Turbellaria	0.1 (0–0.8)	0.0	0.4 (0–1.9)	0.0	1.1 (0–4.7)	0.1 (0–0.2)
Nematoda	5.2 (2.7–11.0)	0.0	4.5 (1.7–6.8)	0.4 (0.3–0.4)	4.3 (0–10.6)	0.4 (0.1–0.7)
Oligochaeta	19.2 (9.2–34.0)	2.8 (1.3–3.8)	7.9 (4.0–15.0)	4.7 (3.9–6.3)	7.4 (2.0–11.2)	5.3 (1.3–7.5)
Acari	2.2 (0–5.7)	0.2 (0–0.6)	3.5 (0.2–7.2)	0.0	2.6 (0–4.8)	0.9 (0.4–1.6)
Gastropoda	0.0	0.0	0.0	0.0	3.6 (2.2–5.3)	5.6 (0–10.1)
Bivalvia	0.0	0.0	0.0	0.0	7.5 (2.2–13.5)	3.1 (0–5.2)
Ephemeroptera	0.0	0.0	0.1 (0–0.4)	0.0	0.5 (0–2.1)	0.0
Plecoptera	4.0 (0.2–9.9)	0.2 (0–0.6)	3.6 (0.3–15.0)	0.2 (0–0.4)	3.0 (0.4–6.7)	0.0
Trichoptera	1.5 (0–4.6)	0.3 (0–0.8)	1.6 (0–4.7)	0.0	0.5 (0–1.0)	0.1 (0–0.2)
Chironomidae	41.0 (32.7–51.4)	41.5 (31.9–56.8)	49.2 (26.5–66.9)	77.0 (68.2–83.7)	40.0 (14.7–67.0)	31.8 (5.8–44.3)
Other Diptera	1.2 (0–3.4)	0.4 (0–1.3)	2.9 (0–8.6)	0.8 (0–2.4)	0.6 (0–1.3)	0.0
Coleoptera	1.3 (0–2.3)	2.5 (1.3–6.3)	0.9 (0–1.6)	0.3 (0–0.4)	1.9 (0.5–4.4)	0.7 (0.4–0.9)
Megaloptera	0.03 (0–0.2)	0.0	0.0	0.0	0.2 (0–1.0)	0.0
Hydra	0.0	0.0	0.0	0.0	0.0	0.7 (0–2.8)

All samples taken in August/September. Sampling periods are indicated in Table 4.

the following years, both species were recorded regularly in the fish food. *Gammarus* was recorded in Lake Svartavasstjørni for the first time in 2000. Two years later *Lepidurus* entered the trout diet in this lake. The results indicate weak populations of both species.

The benthic samples and the colonisation of the jute bags of Lake Svartavatnet and Lake Svartavasstjørni did not give any indication of presence of *Gammarus* and *Lepidurus* (Table 3). Both methods gave samples dominated by Chironomidae, Cladocera and Oligochaeta. The reference Lake Skiftesjøen was different (Table 3). Besides high densities of Cladocera and Chironomidae, *Gammarus* was present at high numbers both in benthic samples and on the jute bags. In the latter this amphipod constituted 28% of all specimens. *Lepidurus* was absent on the jute bags, but recorded annually in benthic samples.

4 Discussion

Due to the increased acidification, the critical limits of both the brown trout populations and the acid-

sensitive fish food animals in the studied area was exceeded in the 1980s. The values measured in 1993, before liming, indicate a water quality harmful to brown trout, *G. lacustris* and *L. arcticus*. After mitigation by liming, the brown trout population densities have increased in both studied lakes. Since *G. lacustris* and *L. arcticus* are vulnerable to grazing by fish (Borgstrøm, Garnås, & Saltveit, 1984; Museth, Borgstrøm, Brittain, Herberg, & Naalsund, 2002), a similar rapid population build-up may be obstructed. The fecundity of both species is low. *G. lacustris* has a 2-year life cycle in the area (Bjerknes, 1974). The females collected in L. Skiftesjøen carried an average number of 22 eggs per female (Fjellheim, Tysse, & Bjerknes, 2002). *L. arcticus* has a short adult life span. The reproductive period is coincident with the main growth period of trout in alpine areas, making it an important factor for fish production and quality (Sømme, 1934). *L. arcticus* start producing eggs in late summer, only one or a few at a time. Reproduction is continuous, but there is no information on the fecundity of the species. The population decline is rapid, but individuals have been found in trout stomachs in January (Sømme, 1934).

Table 4 Occurrence of *Gammarus lacustris* and *Lepidurus arcticus* in benthic samples, jute bags and trout stomachs in Lake Svartavatnet, Lake Svartavasstjørni and the reference Lake Skiftesjøen

: Absence

: Presence

: No record

	Locality	Method	74	85	87	91	95	97	98	99	00	01	02	03	04	
Gammarus lacustris	L. Svartavatnet	Benthic samples														
		Jute bags														
		Trout stomachs														
	L. Svartavasstjørni	Benthic samples														
		Jute bags														
		Trout stomachs														
	L. Skiftesjøen (reference)	Benthic samples														
		Jute bags														
Lepidurus arcticus	L. Svartavatnet	Benthic samples														
		Jute bags														
		Trout stomachs														
	L. Svartavasstjørni	Benthic samples														
		Jute bags														
		Trout stomachs														
	L. Skiftesjøen (reference)	Benthic samples														
		Jute bags														

Data before 1997: after Madsen (1975, 1986, 1988) and Elnan (1991).

Small populations of benthic animals may be difficult to detect using conventional benthic sampling techniques. Due to high mobility, fish should normally have a much higher detection rate of rare and attractive prey. The monitoring of River Audna in southernmost Norway gives an example of this. The freshwater snail *Lymnaea peregra* was first recorded in brown trout stomachs in 1994, 7 years after liming (Raddum & Fjellheim, 2003), while the species was first recorded in the benthic samples in 1996. Runnström and Määr (1950) recorded *L. arcticus* in stomachs of charr, while a large number of benthic samples from the same lake gave negative results. Jute bags were earlier used for capture and transport of *G. lacustris* (Dahl, 1915). The densities in the jute bags from the reference lake demonstrate the attraction to this substrate. Absence of the species in the two limed lakes gives a clear indication of low population densities.

Due to the high selectivity of the fish, mapping of the Norwegian distribution of common freshwater

malacostrachans and notostrachans are partly based on reports from fishermen (Økland, 1980; J. Økland & K. A. Økland, 2002). The technique of using fish as benthic samplers is frequently used in the marine environment, both on the community level and on species level (Frid & Hall, 1999; Link, 2004). Lilly and Parsons (1991) used Atlantic cod in studies of shrimp distribution and abundance. Atlantic sturgeon has been used as a proxy in studies of isopod population dynamics (Rachlin & Warkentine, 1997). The technique is also known from freshwater herbivore fishes (Sellman, Johansen, & Coburn, 2001).

The available information on the presence/absence of *G. lacustris* and *L. arcticus* in the study area, summarized in Table 4, show that our first hypothesis is valid. Examination of fish stomachs is the best method of monitoring low-density populations of attractive prey species. Our second hypothesis is only partly fulfilled. Both species have entered the trout food chain in the lakes, but at present at a very low frequency. The low abundance is probably caused by

a combination low fecundity and high predation pressure.

The increased densities of the trout populations after liming is very good with respect to the genetic conservation of the endangered fine spotted trout. The dense fish populations are, however, not consistent with our goal: a dominance of *Gammarus* and *Lepidurus* in the trout food. These crustaceans are, however, not threatened and viable populations exist in many lakes and ponds of the Hardangervidda. The food chains in the lakes will develop towards a balance between the trout and its common prey. The size of the prey populations will depend upon several factors, of which predation pressure is a key factor.

Benthic samples are normally a good indicator of the presence of *G. lacustris* and *L. arcticus* in dense populations. The distribution of both species may be restricted, due to low density and patchiness. We conclude that studies of fish stomachs are a necessary supplement to benthic samples in monitoring low-density populations of attractive fish food animals.

Acknowledgements The authors gratefully acknowledge the Norwegian Directorate for Nature Management for financing this study. A special thank is given to Herman Stakseng and Gunnar Elnan for help during fieldwork and for collecting additional fish stomach samples. We will also thank two anonymous reviewers for valuable comments to the manuscript.

References

- Aass, P. (1969). Crustacea, especially *Lepidurus arcticus* Pallas, as brown trout food in Norwegian mountain reservoirs. *Rep. Inst. Freshw. Res. Drottningholm*, 49, 183–201.
- Allen, J. A. (1988). Frequency-dependent selection by predators. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, 319, 485–502.
- Berg, M. (1954). New localities of *Lepidurus arcticus* Pallas in North-Norway. *Astarte*, 9, 1–5.
- Bjerknes, V. (1974). Life cycle and reproduction of *Gammarus lacustris* G.O. Sars (Amphipoda) in a lake at Hardangervidda, western Norway. *Norwegian Journal of Zoology*, 22, 39–43.
- Borgstrøm, R. (1970). *Lepidurus arcticus* in the Stolsvatn Reservoir in Hallingdal. *Fauna*, 23, 12–20, Oslo. (In Norwegian, English summary).
- Borgstrøm, R., Brittain, J., & Lillehammer, A. (1976). Invertebrates and acid water. Review of sampling sites. SNSF Project IR 21/76, Oslo-Ås (In Norwegian).
- Borgstrøm, R., Gamås, E., & Saltveit, S. J. (1984). Interactions between brown trout, *Salmo trutta* L., and minnow, *Phoxinus phoxinus* (L.) for their common prey, *Lepidurus arcticus* (Pallas). *Verh. Internat. Verein. Limnol.*, 22, 2548–2552.
- Borgstrøm, R., & Hendrey, G. R. (1976). PH tolerance of the first larval stages of *Lepidurus arcticus* Pallas and adult *Gammarus lacustris* G. O. Sars. SNSF Project IR 22/76, Oslo-Ås.
- Dahl, K. (1915). A study of the biology and distribution of *Gammarus pulex* in Norway. *The Norwegian Association of Hunters and Anglers. Report*, 44, 323–352. (In Norwegian).
- Dahl, J. (1998). The impact of vertebrate and invertebrate predators on a stream benthic community. *Oecologia*, 117, 217–226.
- Dedual, M., Maxwell, I. D., Hayes, J. W., & Strickland, R. R. (2000). Distribution and movements of brown (*Salmo trutta*) and rainbow trout (*Oncorhynchus mykiss*) in Lake Otamangakau, central North Island, New Zealand. *New Zealand Journal of Marine and Freshwater Research*, 34, 629–636.
- Elnan, G. (1991). Test fishing results – Svartavasstjønn 24.07.91. Eidfjord municipality.
- Fjellheim, A., Tysse, Å., & Bjerknes, V. (2001). Reappearance of highly acid-sensitive invertebrates after liming of an alpine lake ecosystem. *Water Air and Soil Pollution*, 130, 1391–1396.
- Fjellheim, A., Tysse, Å., & Bjerknes, V. (2002). *The fine-spotted brown trout at Hardangervidda. – Norwegian directorate for nature management. Report 2002–1*, Trondheim p. 55.
- Frid, C. L. J., & Hall, S. J. (1999). Inferring changes in North Sea benthos from fish stomach analysis. *Marine Ecology. Progress Series*, 184, 83–188.
- Hesthagen, T. (1979). Distribution of *Lepidurus arcticus* in Lom municipality, Oppland County. *Fauna*, 32, 30–33, Oslo. (In Norwegian, English summary).
- Hynes, H. B. N. (1950). The food of freshwater sticklebacks (*Gasterosteus aculeatus* and *Pygosteus pungitius*), with a review of methods used in the studies of the food of fishes. *Journal of Animal Ecology*, 19, 36–58.
- Jensen, K. W. (1977). On the dynamics and exploitation of the population of brown trout, *Salmo trutta* L. in Lake Øvre Heimdalsvatn, Southern Norway. *Rep. Inst. Freshw. Res. Drottningholm*, 56, 18–69.
- Lien, L. (1978). The dynamics and exploitation of the brown trout population of Øvre Heimdalsvatn. In R. Vik (Ed.), *The Lake Øvre Heimdalsvatn, a subalpine freshwater ecosystem – Holarctic Ecology*, 1, 279–300.
- Lilly, G. R., & Parsons, D. G. (1991). Distributional patterns of the northern shrimp (*Pandalus borealis*) in the Northwest Atlantic as inferred from stomach contents of cod (*Gadus morhua*). *Int. Counc. Explor. Sea Comm. Meet.* 1991/ K:41.
- Link, J. S. (2004). Using fish stomachs as samplers of the benthos: Integrating long-term and broad scales. *Marine Ecology. Progress Series*, 269, 265–275.
- Madsen, J. P. (1975). Test fishing in Eidfjord municipality 1974. County Governor of Hordaland.
- Madsen, J. P. (1986). Test fishing in Eidfjord municipality 1985. County Governor of Hordaland.
- Madsen, J. P. (1988). Test fishing in Eidfjord municipality 1987. County Governor of Hordaland.

- McNaught, A. S., Schindler, D. W., Parker, B. R., Paul, A. J., Anderson, R. S., Donald, D. B., et al. (1999). Restoration of the food web of an alpine lake following fish stocking. *Limnology and Oceanography*, 44, 27–136.
- Museth, J., Borgström, R., Brittain, J. E., Herberg, I., & Naalsund, C. (2002). Introduction of the European minnow into a subalpine lake: Habitat use and long-term changes in population dynamics. *Journal of Fish Biology*, 60, 1308–1321.
- Økland, K. A. (1980). Ecology and distribution of *Gammarus lacustris* in Norway. *SNSF Project Internal report* 61/80 Oslo/Ås. Oslo-Ås Norway pp. 1–87. (In Norwegian)
- Økland, K. A., & Økland, J. (1985). Factor interaction influencing the distribution of the freshwater “shrimp” *Gammarus*. *Oecologia*, 66, 364–367.
- Økland, J., & Økland, K. A. (2002). *Findings of Anostraca and Notostraca in Norway* – final report. University of Oslo.
- Pechlaner, R. (1984). Dwarf populations of arctic charr in high-mountain lakes of the Alps resulting from under-exploitation. *Biology of the Arctic charr: Proc. Int. symp. on Arctic charr*, 1984, 319–327.
- Rachlin, J. W., & Warkentine, B. E. (1997). Comments on the population structure of the benthic marine isopod *Politana concharum* collected by the Atlantic sturgeon, *Arcipenser oxyrinchus*. *Crustaceana*, 70, 368–529.
- Raddum, G. G., & Fjellheim, A. (2003). Liming of River Audna, Southern Norway. A large scale experiment of benthic invertebrate recovery. *Ambio*, 32, 230–234.
- Reiriz, L., Níciéza, A. G., & Brana, F. (1998). Prey selection by experienced and naive juvenile Atlantic salmon. *Journal of Fish Biology*, 53, 100–114.
- Runnström, S., & Määr, A. (1950). *Lepidurus arcticus* Pallas in Indalsälven and Faxälven watersystems, Sweden and Norway. *Rep. Inst. Freshw. Res. Drottningholm*, 31, 147–150.
- Salvanes, A. G. V., & Hart, P. J. B. (1998). Individual variability in state-dependent feeding behaviour in three-spined sticklebacks. *Animal Behaviour*, 55, 1349–1359.
- Sellman, S. M., Johansen, J. R., & Coburn, M. M. (2001). Using fish to sample diatom composition in streams: Are intestinal floras representative of natural substrates? *Journal of Phycology*, 37, 44–44.
- Skaala, Ø., & Jørstad, K. (1987). Fine-spotted brown trout (*Salmo trutta*); its phenotypic description and biochemical genetic variation. *Canadian Journal of Fisheries and Aquatic Sciences*, 44, 1775–1779.
- Sweka, J. A., & Hartman, K. L. (2001). Influence of turbidity on brook trout reactive distance and foraging success. *Transactions of the American Fisheries Society*, 130, 138–146.
- Sømme, S. (1934). Contributions to the biology of Norwegian fish food animals. 1. *Lepidurus arcticus* Pallas 1793. Syn. *L. glacialis* Krøyer 1847. *The Norwegian Academy of Sciences and Letters. Dissertations* 1934, no. 6, 1–36.
- Warburton, K. (2003). Learning of foraging skills by fish. *Fish and Fisheries*, 4, 203–215.

Acidification at Plastic Lake, Ontario: Has 20 Years Made a Difference?

Shaun A. Watmough · Julian Aherne ·
M. Catherine Eimers · Peter J. Dillon

Received: 17 June 2005 / Accepted: 3 April 2006 / Published online: 14 February 2007
© Springer Science + Business Media B.V. 2007

Abstract In response to reduced sulphur emissions, there has been a large decrease in sulphate (SO_4^{2-} ; $-0.97 \mu\text{eq l}^{-1} \text{ year}^{-1}$) and hydrogen ($-1.18 \mu\text{eq l}^{-1} \text{ year}^{-1}$) ion concentration in bulk precipitation between 1980 and 2000 at Plastic Lake in central Ontario. The benefit of this large reduction in SO_4^{2-} deposition on stream water chemistry was assessed using the gauged outflow from a conifer-forested catchment (PC1; 23.3 ha), which is influenced by a small wetland located immediately upstream of the outflow. Sulphate concentrations declined, but not significantly due to large inter-annual variation in SO_4^{2-} concentration. Between 1980 and 2000, there were significant increases in dissolved organic carbon, ammonium and potassium concentration likely reflecting increased mineralisation in the wetland. Calcium concentrations in PC1 decreased during the two decade period ($-2.24 \mu\text{eq l}^{-1} \text{ year}^{-1}$), as a consequence there was no improvement in stream pH and the Ca:Al ratio in PC1 continued to decline. A similar response was noted in an upland-draining sub-

catchment of PC1-08 that has been monitored since 1987. Despite large reductions in SO_4^{2-} deposition and almost complete retention of nitrogen in soil, there has been no improvement (in terms of pH) in stream water at PC1 due to a combination of soil acidification and climatic (droughts, increased mineralisation) perturbations.

Keywords acidification · aluminium · calcium · climate · recovery · sulphate

1 Introduction

Acid rain is recognised as a major environmental concern in eastern Canada and since the late 1970s sulphur dioxide (SO_2) emissions in Canada and the United States have decreased in response to various legislation (e.g., the Acid Rain Control Program, 1985; and the Canada–U.S. Air Quality Agreement, 1991). Nevertheless, recent critical load estimates indicate that large areas of forest (52% of forest in eastern Canada; Ouimet, Arp, Watmough, Aherne, & Demerchant, 2006) and large numbers of lakes in eastern Canada currently receive acid deposition in excess of the critical load (Jeffries & Ouimet, 2005). Jeffries et al. (2003) recently reported that despite substantial reductions in SO_2 emission since 1980 there has been limited improvement in pH and alkalinity. In Ontario for example, only 13% of 662 lakes analysed exhibited an increase in pH during the

S. A. Watmough (✉) · J. Aherne · P. J. Dillon
Environmental and Resource Studies, Trent University,
1600 West Bank Drive,
Peterborough, ON K9J 7B8, Canada
e-mail: swatmough@trentu.ca

M. C. Eimers
Department of Geography, Trent University,
Peterborough, ON K9J 7B8, Canada

1990s. In part, this delay in chemical recovery may be due to continued soil acidification (Watmough & Dillon, 2003), although increased organic acid export or climate induced releases of SO_4^{2-} or nitrate (NO_3^-) may also delay chemical recovery of forest soils and surface waters (Eimers & Dillon, 2002; Evans, Freeman, Monteith, Reynolds, & Fenner, 2002; Watmough, Eimers, Aherne, & Dillon, 2004). Chemical recovery of surface waters from acidification has been reported in other parts of the world where emission reductions have occurred. In a comprehensive review of surface water data from 12 geographical regions in Europe and North America, Skjelkvale et al. (2005) reported that improvements in pH and alkalinity are widely observed in response to emission control programs and decreasing acidic deposition. Given that the implementation of emission reductions is extremely costly it is important to characterise the impact of acid deposition on sensitive ecosystems and identify reasons for the delay of (or lack of) chemical and subsequent biological recovery in Ontario.

In an attempt to assess the impact of reduced SO_2 emissions in eastern Canada in recent decades, we report elemental fluxes in bulk deposition and stream export from a forested catchment (PC1) containing a small *Sphagnum*-conifer swamp in central Ontario for the periods 1980–85 and 1995–2000. We also report elemental export from an upland sub-catchment (PC1-08) for the years 1989–1991 and 1999–2001.

2 Materials and Methods

2.1 Study Site

Plastic Lake (PC) is located in Haliburton County on a southern extension of the Precambrian Shield in central Ontario, Canada (45°11' N, 78°50' W), and is typical of acid-sensitive lakes in this region. The 32 ha headwater lake is fed by one major stream (PC1) and six ephemeral streams, which together drain an area of approximately 90 ha. Plastic Lake-1 (PC1) is the largest sub-catchment (23.3 ha) in the watershed, and is characterised by thin (average depth 0.37 m to bedrock) orthic humo-ferric and ferro-humic podzols, formed from thin, sandy basal tills (Neary, Mistray, & Vanderstar, 1987). The uneven-aged forest at PC1 is dominated by white pine (*Pinus strobus* L.), eastern hemlock (*Tsuga canadensis* L.),

red oak (*Quercus rubra* L.), red maple (*Acer rubrum* L.) and large toothed aspen (*Populus grandidentata* Michx.) in the upland areas, and by white cedar (*Thuja occidentalis* L.) and black spruce (*Picea mariana* (Mill.) BSP) in the swamp regions. A 2.2 ha conifer-*Sphagnum* swamp is located approximately 50 m above the catchment outflow and more than 85% of the runoff from the PC1 catchment drains through the swamp before discharging to Plastic Lake. A short (<250 m) ephemeral stream (PC1-08), which has been monitored periodically since 1987, drains the northeastern part of PC1 before discharging into the swamp.

2.2 Bulk Deposition

Deposition data were obtained from collections of bulk deposition, defined as that caught in a continuously open, 0.25 m² collector. The collectors were fitted with Teflon-coated funnels that are screened (80 µm Nitex mesh) to prevent contamination by insects and debris. Precipitation samples were removed from collectors when there was sufficient volume for chemical analyses, typically weekly. Analytical methods for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , NO_3^- and NH_4^+ are outlined in detail in Ontario Ministry of Environment (1983) and were unchanged during the study period. Briefly, base cations were measured by atomic absorption spectrophotometry, SO_4^{2-} by ion chromatography and NH_4^+ and NO_3^- were determined colourimetrically. Precipitation volume and volume-weighted concentrations were calculated for each water year (June 1–May 31). On the rare occasions when data were missing the average precipitation values from three nearby (within 50 km) bulk collectors (or stream flow from nearby weirs with highly correlated discharge relationships) were used.

2.3 Stream Export

Water level or stage was recorded continuously at a V-notched weir installed at the catchment outflow (PC1) and PC1-08, and daily stream discharge (m³ day⁻¹) was computed using established stage–discharge relationships (Hutchinson, Scott, Futter, & Morgan, 1994). Water samples for chemical analyses were collected at the weir at regular intervals (at least biweekly) when there was flow, although sampling

was more frequent during the spring melt period. Water samples were filtered through 80 μm Nitex mesh in the field, and transported to the laboratory for chemical analyses in insulated containers. Filters (Nitex mesh) were rinsed in deionised water in the laboratory and rinsed in stream water immediately prior to sampling. Samples were analysed for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , NO_3^- and NH_4^+ as outlined above. In addition, samples were analysed for Kjeldahl N (TKN) and dissolved organic carbon (DOC) using standard methods (Ontario Ministry of Environment, 1983). The contribution of organic acids to the ion balance was estimated from measured DOC concentrations and pH (Oliver, Thurman, & Malcolm, 1983). Labile monomeric aluminium (Al^{3+}) concentrations in PC1 and PC1-08 were only determined for a short period of time during the study (1985–1995) LaZerte, Chun, Evans and Tomassini (1988) and relationships between H^+ and Al^{3+} in PC1 and PC1-08 were used to estimate Al^{3+} concentration outside this period. These estimates were based on a generalisation of the accepted gibbsite H–Al relationship.

$$[\text{Al}] = K_{\text{Allox}} [\text{H}]^a$$

where $K_{\text{Allox}}=0.38$, $a=1.27$, $r^2=0.51$ (PC1-08) and $K_{\text{Allox}}=0.20$, $a=0.86$ (PC1), $r^2=0.40$.

A Seasonal Kendall test (treating months as seasons) was used to determine trends in stream water

and bulk deposition chemistry (Hirsch & Slack, 1984). This method was chosen as it is robust against seasonality, missing values and autocorrelation and has been used extensively for assessing the chemical response of surface waters to declining acid deposition (e.g. see Hydrology and Earth System Sciences, 2001, vol. 5). In order to facilitate comparison of data at the beginning and end of the study period and to reduce the impact of year-to-year variation in chemistry data 5 year average volume-weighted values for 1980–1985 and 1995–2000 are presented.

3 Results and Discussion

3.1 Trends in Deposition and Stream Chemistry

Between 1980 and 2000, SO_4^{2-} concentration in bulk precipitation at PC1 has declined by approximately 30% (Table 1). Five-year annual average SO_4^{2-} concentrations (1980/85) were $61.3 \mu\text{eq l}^{-1}$ compared with $42.1 \mu\text{eq l}^{-1}$ (1995–2000) (Table 1). The large decrease in SO_4^{2-} was almost completely balanced by large reductions in H^+ concentration, which decreased from 62.0 to $41.1 \mu\text{eq l}^{-1}$ over the same time period (Table 1). There were small decreases in Na^+ and Cl^- concentration but no significant change in concentration of any of the other major ions (Table 1). The large reduction in SO_4^{2-} and H^+ ion concentration typifies recent reports in eastern North America and

Table 1 Mean annual volume-weighted major anion and cation concentrations in bulk deposition and PC1 outflow in 1980–85 and 1995–2000

	Bulk deposition			PC1		
	1980/85	1995/00	Trend	1980/85	1995/00	Trend
SO_4^{2-}	61.3	42.1	−0.97***	158.1	116.3	n.s.
NO_3^-	36.1	37.4	n.s.	1.7	1.5	n.s.
Cl^-	4.0	3.6	−0.05*	9.4	10.3	n.s.
DOC	n.d.	n.d.	n.d.	8.3	10.3	+0.13**
H^+	62.0	41.1	−1.18***	46.5	41.9	n.s.
Ca^{2+}	13.4	11.8	n.s.	105.3	68.4	−2.24*
Mg^{2+}	3.7	3.3	n.s.	39.7	30.1	n.s.
K^+	1.8	1.6	n.s.	3.2	4.2	+0.10*
Na^+	2.8	2.4	−0.04*	22.5	24.8	n.s.
NH_4^+	24.8	26.5	n.s.	0.3	0.9	+0.03*
PPT/Q	1.07	0.98	n.s.	0.62	0.54	n.s.

* $p<0.05$; ** $p<0.01$; *** $p<0.001$; n.s. not significant ($p<0.05$); n.d. not measured.

Units: $\mu\text{eq l}^{-1}$, except Dissolved Organic Carbon (DOC: mg l^{-1}) and rainfall and runoff volume (PPT and Q: m). Significant trends and annual slope between 1980 and 2000 are shown.

Europe and reflects the success of programs implemented to reduce SO_2 emissions (Hedin et al., 1994). In some areas (or over certain time periods) part of the benefit of reduced SO_4^{2-} deposition has been offset by decreased base cation deposition (Hedin et al., 1994), although this is not the case at PC1 where the reduction in SO_4^{2-} has produced an equivalent reduction in H^+ concentration.

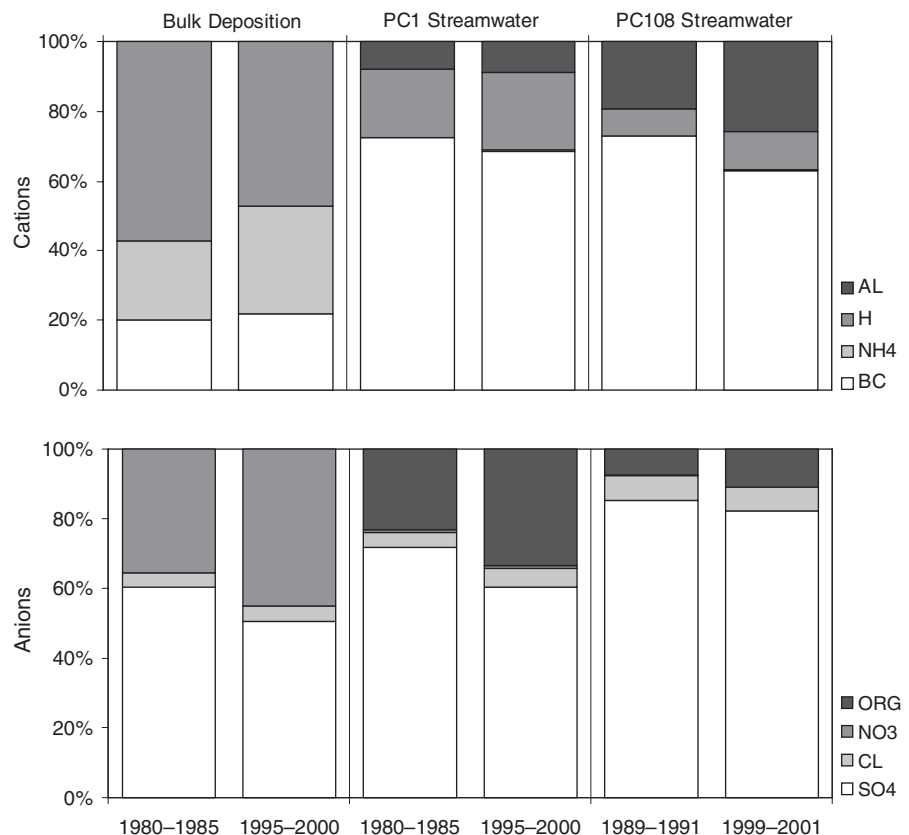
The annual average SO_4^{2-} concentration in PC1 was $158.1 \mu\text{eq l}^{-1}$ in 1980/85 period compared with $116.3 \mu\text{eq l}^{-1}$ in the 1995/00 period, a reduction of 26%, which is similar in magnitude to the SO_4^{2-} reduction in bulk deposition (Table 1). However there was no significant monotonic trend in SO_4^{2-} detected due to large inter-annual variations in SO_4^{2-} concentration that occur as a result of drought-induced SO_4^{2-} release from the wetland (Eimers & Dillon, 2002). During summer droughts, sulphur stored in the wetland is re-oxidised as the water table drops and the SO_4^{2-} is released when rains resume (Eimers & Dillon, 2002).

There was a significant increase in DOC, NH_4^+ and K^+ concentration in PC1 between 1980 and 2000

(Table 1). At PC1, there has been no net increase in forest biomass and the 1980s and 1990s were the warmest two decades on record (IPCC, 2001), which will likely stimulate mineralisation in the wetland and lead to increased DOC, NH_4^+ and K^+ leaching. Several studies in Europe and eastern North America have reported increased concentrations of DOC (Driscoll, Driscoll, Roy, & Mitchell, 2003; Evans et al., 2005), although the cause of the increases remains under debate. For example, the increases in DOC may be caused by climate warming and increased mineralisation or declining SO_4^{2-} concentrations (acidity and/or ionic strength) (Clark, Chapman, Adamson, & Lane, 2005; Evans et al. 2005; Hejzlar et al., 2003; Krug & Frink, 1983).

Between 1980 and 2000 there was a large, significant decline in Ca^{2+} concentration in PC1 ($-2.24 \mu\text{eq l}^{-1} \text{ year}^{-1}$); annual average Ca^{2+} concentrations decreased from $105.3 \mu\text{eq l}^{-1}$ in the 1980/85 period to $68.4 \mu\text{eq l}^{-1}$ in the 1995/00 period, a decrease of 35% (Table 1). The decrease in Ca^{2+} has almost completely offset the reduction in SO_4^{2-} concentration and as a result there has been no

Fig. 1 Mean annual cation (upper) and anion (lower) balance (%) in bulk precipitation and PC1 stream water during the periods 1980–1985 and 1995–2000; and PC1-08 stream water during the periods 1989–1991 and 1999–2001



significant decrease in H^+ ion concentration over the two-decades (Table 1). The large decrease in Ca^{2+} is likely attributed to continued soil acidification at PC1 (Watmough & Dillon, 2003). Mass balance estimates indicate that Ca^{2+} leaching from PC1 exceeds the combined Ca^{2+} inputs from deposition and mineral weathering leading to a decline in exchangeable soil Ca^{2+} , which was supported by repeated field measurements in 1983 and 1999 (Watmough & Dillon, 2003). Declining exchangeable soil Ca^{2+} will result in a greater than expected decline in stream Ca^{2+} in response to declining SO_4^{2-} concentrations (Kirchner & Lydersen, 1995). Despite high concentrations of NO_3^- and NH_4^+ in bulk deposition, NO_3^- concentrations in PC1 (and PC1-08) are very low ($<5 \mu eq l^{-1}$) and have not increased over the 20-year period (Table 1).

3.2 Ion Budgets

In 1980/85 SO_4^{2-} was the dominant anion in bulk deposition, accounting for 60% of the anions in bulk deposition (Fig. 1). At the end of the study period (1995/00), SO_4^{2-} and NO_3^- were present in approximately equivalent amounts reflecting the increasing relative importance of NO_3^- deposition as sulphur emissions decline in eastern North America. In 1980/85 H^+ was the dominant cation in precipitation, accounting for almost 60% of the total cations (Fig. 1). However, by the end of the study period, H^+ represented less than half of the total cations, reflecting the improvement in atmospheric deposition.

In contrast to bulk deposition, SO_4^{2-} and organic anions are dominant in stream water, but the relative contribution of SO_4^{2-} in PC1 declined over the study period reflecting the change in SO_4^{2-} deposition (Fig. 1). At the PC1-08 upland draining stream between 1989/91 and 1999/01 the magnitude of chemical change was smaller due to the shorter time period considered and the contribution of organic anions was lower (Fig. 1). Despite reductions in SO_4^{2-} , the relative contribution of both H^+ and Al^{3+} to the cation balance in PC1 increased slightly (even though there was no change in H^+ and Al^{3+} concentration) due to the large decrease in Ca^{2+} concentration. A decline in Ca^{2+} concentration was also noted in PC1-08 between 1989/91 and 1999/01 (Fig. 1).

3.3 Calcium: Aluminum Ratios in PC1 and PC1-08

Critical load calculations for forest soils usually set a critical acid neutralising capacity leaching based on a molar ratio of base cations or calcium to aluminium in soil solution. Cronan and Grigal (1995) suggested that there is a risk of adverse impacts on tree growth or nutrition when the soil solution Ca:Al molar ratio ≤ 1.0 . Although the use of critical chemical limits has been the subject of great debate, the Ca:Al ratio can be considered to be an indicator of the acid status of forest soils. Because there has been a large decline in Ca^{2+} concentration in both PC1 and PC1-08 streams and no change in H^+ concentration, estimated Ca:Al molar ratios (Al estimated using H–Al relationships) in both PC1 and PC1-08 have decreased during the study period (Fig. 2). It should be noted that error associated with estimation of Al^{3+} from pH (H^+) will be constant throughout the study period. Ca:Al ratios in PC1 were higher than in PC1-08 due to the large influence of the wetland and decreased from between approximately 8 and 10 in the early 1980s to as low as 5 by the end of the study period. Ca:Al ratios in PC1-08 decreased from approximately four in the mid-1980s to values around two at the end of the study period. While these values are higher than the critical values reported by Cronan and Grigal (1995) and there

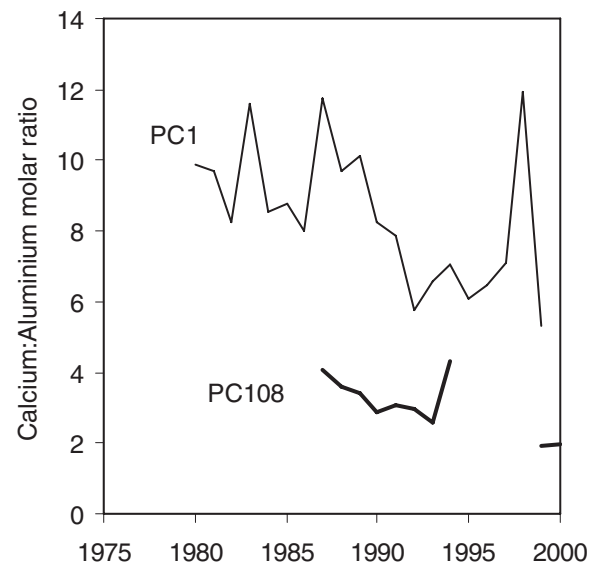


Fig. 2 Temporal trend in calcium:aluminium molar ratio for PC1 (thin line) and PC1-08 (thick line) for the period 1980–2000. Relationship between H–Al was used to predict the temporal trend for labile monomeric aluminium (see text)

is some uncertainty in the estimates based on pH measurements, it is possible that Ca:Al ratios in mineral soil may be approaching values that pose a risk to forest health.

4 Conclusion

Despite large reductions in SO_4^{2-} and corresponding decreases in H^+ ion concentration in bulk deposition there has been little improvement in the chemical status of streams at PC between 1980 and 2000 and Ca:Al ratios in stream water continue to decline. In addition, any further increases in organic acid release or future increased NO_3^- leaching could potentially offset the benefits of predicted further declining SO_4^{2-} concentrations and the chemical and subsequent biological recovery at PC1 could be further delayed.

Acknowledgements The authors acknowledge the hard work of staff at the Dorset Environmental Science Centre and the Ontario Ministry of Environment.

References

- Clark, J. M., Chapman, P. J., Adamson, J. K., & Lane, S. N. (2005). Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Global Change Biology*, 11, 791–809.
- Cronan, C. S., & Grigal, D. F. (1995). Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. *Journal of Environmental Quality*, 24, 209–226.
- Driscoll, C. T., Driscoll, K. M., Roy, K. M., & Mitchell, M. J. (2003). Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. *Environmental Science and Technology*, 37, 2036–2042.
- Eimers, M. C., & Dillon, P. J. (2002). Climate effects on sulphate flux from forested catchments in south-central Ontario. *Biogeochemistry*, 61, 337–355.
- Evans, C. D., Freeman, C., Monteith, D. T., Reynolds, B., & Fenner, N. (2002). Climate change – terrestrial export of organic carbon: Communication arising. *Nature*, 415, 862.
- Evans, C. D., Monteith, D. T., & Cooper, D. M. (2005). Long term increases in surface water dissolved organic carbon, possible causes and environmental impacts. *Environmental Pollution*, 137, 55–71.
- Hedin, L. O., Granat, L., Likens, G. E., Buishand, T. A., Galloway, J. N., Butler, T. J., et al. (1994). Steep declines in atmospheric base cations in regions of North America. *Nature*, 367, 351–354.
- Hejzlar, J., Dubrovsky, M., Buchtele, J., & Ruzicka, M. (2003). The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malse River, South Bohemia). *Science of the Total Environment*, 310, 143–152.
- Hirsch, R. M., & Slack, J. R. (1984). A nonparametric trend test for seasonal data with serial dependence. *Water Resources Research*, 20, 727–732.
- Hutchinson, B. A., Scott, L. D., Futter, M. N., & Morgan, A. (1994). Hydrology data for lakes and catchments in Muskoka/Haliburton (1980–1992). Ontario Ministry of Environment data report DR93/5, ISBN 0-7778-2535-X PIBS 3017 17pp.
- IPCC (2001). Third Assessment Report: Climate Change 2001.
- Jeffries, D. S., Clair, T. C., Couture, S., Dillon, P. J., Dupont, J., Keller, W., et al. (2003). Assessing the recovery of lakes in southeastern Canada from the effects of acid deposition. *Ambio*, 32, 176–182.
- Jeffries, D. S., & Ouimet, R. (2005). Critical loads: Are they being exceeded? In H. A. Morrison (Ed.), *Canadian acid deposition science assessment*. Canada: Environment Canada.
- Kirchner, J. W., & Lydersen, E. (1995). Base cation depletion and potential long-term acidification of Norwegian catchments. *Environmental Science and Technology*, 29, 1953–1960.
- Krug, E. C., & Frink, C. R. (1983). Acid rain on acid soil: A new perspective. *Science*, 221, 520–525.
- LaZerte, B. D., Chun, C., Evans, D., & Tomassini, F. (1988). Measurement of aqueous aluminum species: Comparison of dialysis and ion-exchange techniques. *Environmental Science and Technology*, 22, 1106–1108.
- Neary, A. J., Mistray, E., & Vanderstar, L. (1987). Sulphate relationships in some central Ontario forest soils. *Canadian Journal of Soil Science*, 67, 341–352.
- Oliver, B. G., Thurman, E. M., & Malcolm, R. L. (1983). The contribution of humic substances to the acidity of colored natural waters. *Geochimica et Cosmochimica Acta*, 47, 2031–2035.
- Ontario Ministry of the Environment (1983). *Handbook of analytical methods for environmental samples*. Rexdale, Ontario, Canada.
- Ouimet, R., Arp, P., Watmough, S., Aherne, J., & Demerchant, I. (2006). Determination and mapping of critical loads and exceedances for upland forest soils in Eastern Canada. *Water, Air, & Soil Pollution*, 172, 57–66.
- Skjelkvale, B. A., Stoddard, J. L., Jeffries, D. S., Torseth, K., Hogasen, T., Bowman, J., et al. (2005). Regional scale evidence for improvements in surface water chemistry 1990–2001. *Environmental Pollution*, 137, 165–176.
- Watmough, S. A., & Dillon, P. J. (2003). Major element fluxes from a coniferous catchment in central Ontario, 1983–1999. *Biogeochemistry*, 67, 369–398.
- Watmough, S. A., Eimers, M. C., Aherne, J., & Dillon, P. J. (2004). Climate effects on nitrate export from forested catchments in south-central Ontario. *Environmental Science and Technology*, 38, 2383–2388.

Modeling Acidification Recovery on Threatened Ecosystems: Application to the Evaluation of the Gothenburg Protocol in France

David Moncoulon · Anne Probst · Liisa Martinson

Received: 17 June 2005 / Accepted: 15 February 2006 / Published online: 27 January 2007
© Springer Science + Business Media B.V. 2007

Abstract To evaluate the acid deposition reduction negotiated for 2010 within the UNECE LRTAP Gothenburg Protocol, sulphur and nitrogen deposition time-series (1880–2100) were compared to critical loads of acidity on five French ecosystems: Massif Central basalt (site 1) and granite (2); Paris Bassin tertiary sands (3); Vosges mountains sandstone (4) and Landes eolian sands (5). The SAFE model was used to estimate the response of soil solution pH and $\frac{[Al]}{[BC]}$ ratio to the deposition scenario. Among the five sites, critical loads were exceeded in the past at sites 3, 4 and 5. Sites 3 and 4 were still expected to exceed in 2010, the Protocol year. Further reduction of atmospheric deposition, mainly nitrogen, would be needed to achieve recovery on these ecosystems. At sites 3, 4 and 5, the delay

between the critical load exceedance and the violation of the critical chemical criterion was estimated to be 10 to 30 years in the top soil and 50 to 90 years in the deeper soil. At site 5, a recovery was expected in the top soil in 2010 with a time lag of 10 years. Unexpectedly, soil pH continued to decrease after 1980 in the deeper soil at sites 2 and 5. This time lag indicated that acidification moved down the soil profile as a consequence of slow base cation depletion by ion exchange. This delayed response of the soil solution was the result of the combination of weathering rates and vegetation uptake but also of the relative ratio between base cation deposition and acid compounds.

Keywords acidification · atmospheric deposition · France · recovery · SAFE model

D. Moncoulon · A. Probst (✉)
Laboratoire des Mécanismes de Transfert en Géologie,
UMR 5563, CNRS-IRD-Université Paul Sabatier,
14 avenue Edouard Belin, 31400 Toulouse, France
e-mail: anne.probst@ensat.fr

L. Martinson
Lund University Centre for Sustainability Studies,
P.O. Box 170, 221 00 Lund, Sweden

Present address:

A. Probst
ECOLAB UMR 5245,
CNRS-INPT-Université Paul Sabatier,
ENSAT Avenue de l'Agrobiopole,
BP 32607 Auzeville, Tolosane,
31326 Castanet, Tolosan, Cedex, France

1 Introduction

Acidification of soil and water, following the significant increase in sulphur and nitrogen deposition on terrestrial and aquatic ecosystems have been evidenced by many authors in North and Central Europe since the 1970s (e.g. Blank, 1985; Wright & Snekvik, 1978). In France, the exposed areas were located in the Center, North and North-East of the country (Landmann & Bonneau, 1995; Probst, Massabuau, Probst, & Fritz, 1990). The most threatened ecosystems were mainly characterized by low soil weathering rate and the important buffering effect of atmospheric base cation

deposition as well as base cation uptake due to forest productivity on French ecosystems has previously been estimated (Moncoulon, Probst, & Party, 2004). Since the 1980s, a series of protocols under the UN/ECE Convention on Long-Range Transboundary Air Pollution (LRTAP) have been negotiated to reduce atmospheric pollution over Europe. Sulphur deposition has reduced by 83% between 1980 and 2005 in metropolitan France. Over the same period, NO_3 decreased by 33% and NH_4 remained constant (CITEPA, 2003). Since 1999, a new protocol for sulphur and nitrogen (the so-called Gothenburg protocol) has been negotiated to reduce these emissions by the year 2010. In this post-acidification context, to determine the ecosystem behaviour, five representative sites of the French territory were chosen. The objectives of this study were (1) to identify among five ecosystems, which have been exposed to a critical acid pollution in the last decades; (2) to estimate the effects of acid pollution decrease on these ecosystems, estimated by calculating the pH and $\frac{[\text{Al}]}{[\text{BC}]}$ ratio in the soil solution; (3) to evaluate the acid deposition reductions negotiated within the Gothenburg protocol. Critical loads were defined as “the quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to the present knowledge” (Nilsson & Grennfelt, 1988). To achieve our goals, acid atmospheric deposition time series over the 1880–2100 period have been compared to critical loads to determine the exceedance areas. Dynamic modelling has been applied to evaluate the impact of acidification on soil chemical criteria and recovery.

2 Material and Methods

2.1 Site Description

A new ecosystem classification has been set up at the French territory scale to integrate soil, bedrock and vegetation data for critical load calculations. 281 ecosystems have been defined among which 241 concern forests (Moncoulon et al., 2004). In order to take into account the variability of the French ecosystem sensitivity to acidification, five sites were selected, reflecting different combinations of bedrocks, soils and

vegetation species (Table 1). Sites 1 and 2, located in the Massif Central, were both subjected to Mediterranean influence and remoteness from highest pollution sources but differed strongly by their bedrock types (basalt and granite). Site 3, in the Center of France, was close to pollution sources and characterized by inert parent material (sand) and remoteness from Mediterranean influence. Site 4 was closer to high pollution sources from Central Europe, and characterized by sandstoneous bedrock type. Site 5, a sandy soil located near the Atlantic Ocean, receive high seasalt cations and was far from high pollution sources. The vegetation on sites 1, 2, 3 and 4 was planted by deciduous forest whereas on site 5, the forest was coniferous.

2.2 Critical Load Calculation

Critical loads were calculated at the five sites using a mass balance approach in steady state conditions for the soil solution down to one meter soil depth (Hettelingh, Posch, & De Amet, 2001). For each ecosystem, one indicator species was chosen (Table 1). The critical limiting value of pH and $\frac{[\text{Al}]}{[\text{BC}]}$ were determined from soil solution of French ICP Forest network for non significant health effect on trees: $[\text{H}^+]_{\text{crit}} = 25 \mu\text{eq l}^{-1}$, which corresponded to $\text{pH} = 4.6$ and $\frac{[\text{Al}]}{[\text{BC}]} = 1.2$ (Moncoulon et al., 2004; Party, 1999). This value, which corresponded to coniferous conditions (*Picea abies* L.) was used for the acid forest soils in general. However a comparison has been also performed with the critical limits for $\frac{[\text{Al}]}{[\text{BC}]}$, specific of the different plant species, found in the literature (Sverdrup & Warfvinge, 1993). The critical deposition of sulfur was calculated as:

$$\text{CL}_{\text{max}}(\text{S}) = \text{BC}_{\text{dep}} + \text{BC}_{\text{weath}} - \text{BC}_{\text{upt}} - \text{Ac}_{\text{le(crit)}} \quad (1)$$

$$\begin{aligned} \text{Ac}_{\text{le(crit)}} = & -Q \times [\text{H}^+]_{\text{crit}} - 1.2 \times \left(\frac{[\text{Al}]}{[\text{BC}]} \right)_{\text{crit}} \\ & \times (Q \times [\text{BC}]) \end{aligned} \quad (2)$$

To determine the critical load for nitrogen, sulphur deposition had to be fixed. If sulfur deposition was equal to critical load:

$$\text{Cl}_{\text{min}}(\text{N}) = \text{N}_{\text{imm}} + \text{N}_{\text{upt}} \quad (3)$$

Table 1 Description and location of the five studied sites

Site	1	2	3	4	5
Location	Massif Central	Massif Central	Paris bassin	Vosges mountains	Landes
Bedrock	Basalt	Granite	Tertiary sands	Sandstone	Eolian sands
Soil	Andosol	Dystric cambisol	Podzoluvisol	Podzol	Podzol
Indicator species	<i>Fagus sylvatica</i> L.	<i>Quercus humilis</i> Mil.	<i>Carpinus betulus</i> L.	<i>Fagus sylvatica</i> L.	<i>Pinus pinaster</i> Ait.
Forest acid soil $\frac{[Al]}{[BC]}$ critical ratio	1.2	1.2	1.2	1.2	1.2
$\frac{[Al]}{[BC]}$ critical ratio for the indicator species	1.6	1.6	0.85	1.6	0.85

If there was no sulfur deposition:

$$CL_{\max}(N) = N_{\text{imm}} + N_{\text{upt}} + CL_{\max}(S)/(1 - F_{\text{de}}) \quad (4)$$

CL was the critical load, BC base cation, $_{\text{dep}}$ atmospheric deposition, $_{\text{weath}}$ weathering rate, $_{\text{upt}}$ vegetation uptake, $_{\text{crit}}$ critical limit, Ac_{le} acidity leached, Q flux of water percolating in the soil, $_{\text{imm}}$ immobilisation, F_{de} denitrification factor (0 to 1). All fluxes were $\text{eq ha}^{-1} \text{ year}^{-1}$.

2.3 Determination of Exceedance

Exceedance was determined by comparing sulfur and nitrogen deposition to critical loads of sulfur and nitrogen (UBA, 2004) calculated with different critical limits. Deposition pairs (S and N) was plotted in Fig. 1 and compared with the critical load functions, which represented the link between the three critical loads on the (S, N) graph. On each point of the critical load function, the pollutant pair (S and N) represented a critical acid deposition. Exceedance existed if the plot was in region 2 of the graph (over the critical load function) for the chosen indicator species.

2.4 The SAFE Model

SAFE was a dynamic process-oriented multi-layer soil chemistry model (Warfvinge, Falkengren-Grerup, & Sverdrup, 1993), which simulated long-term reaction of the soil solution chemistry to atmospheric deposition. Cation exchange reactions and dissolution rate of 14 specific minerals using kinetic rate laws were considered. Weathering was related to soil solution chemistry. SAFE required time-series of input data regarding nutrient uptake and cycling, which could be derived

using the MAKEDEP model (Alveteg, Walse, & Warfvinge, 1998). Plant uptake was determined in relation to forest management. Several basic assumptions have been done in the model development: sulphate adsorption was not taken into account; gibbsite equilibrium was used to describe the concentrations of aluminium; all base cations were considered divalents; all N was supposed to be present as NO_3^- , assuming complete and immediate nitrification in the soil. In this study, the SAFE model was used on a 200 year period (1900–2100). The S and N atmospheric deposition followed a site-specific scenario. Base cation deposition was considered as constant over the period since no data on historical variations exist. Soil solution parameters were simulated by the model and calibration was done using the base saturation value in 1995. SAFE was calibrated by varying the initial base saturation until an agreement between measurements and SAFE calculations was achieved for each soil layer.

2.5 Input Data

2.5.1 Atmospheric Deposition

Two datasets of atmospheric deposition were used: (1) the EMEP model deposition data for acid deposition time series and (2) the French ICP Forest RENECOFOR network data to determine present-day base cations and chloride deposition.

EMEP deposition time-series EMEP was a European network, which collected and centralised deposition data from national networks. The EMEP model was an acid deposition Lagrangian model (Iversen, 1993). In France, EMEP used eight stations for measurements of acid compounds in wet and dry deposition. The EMEP

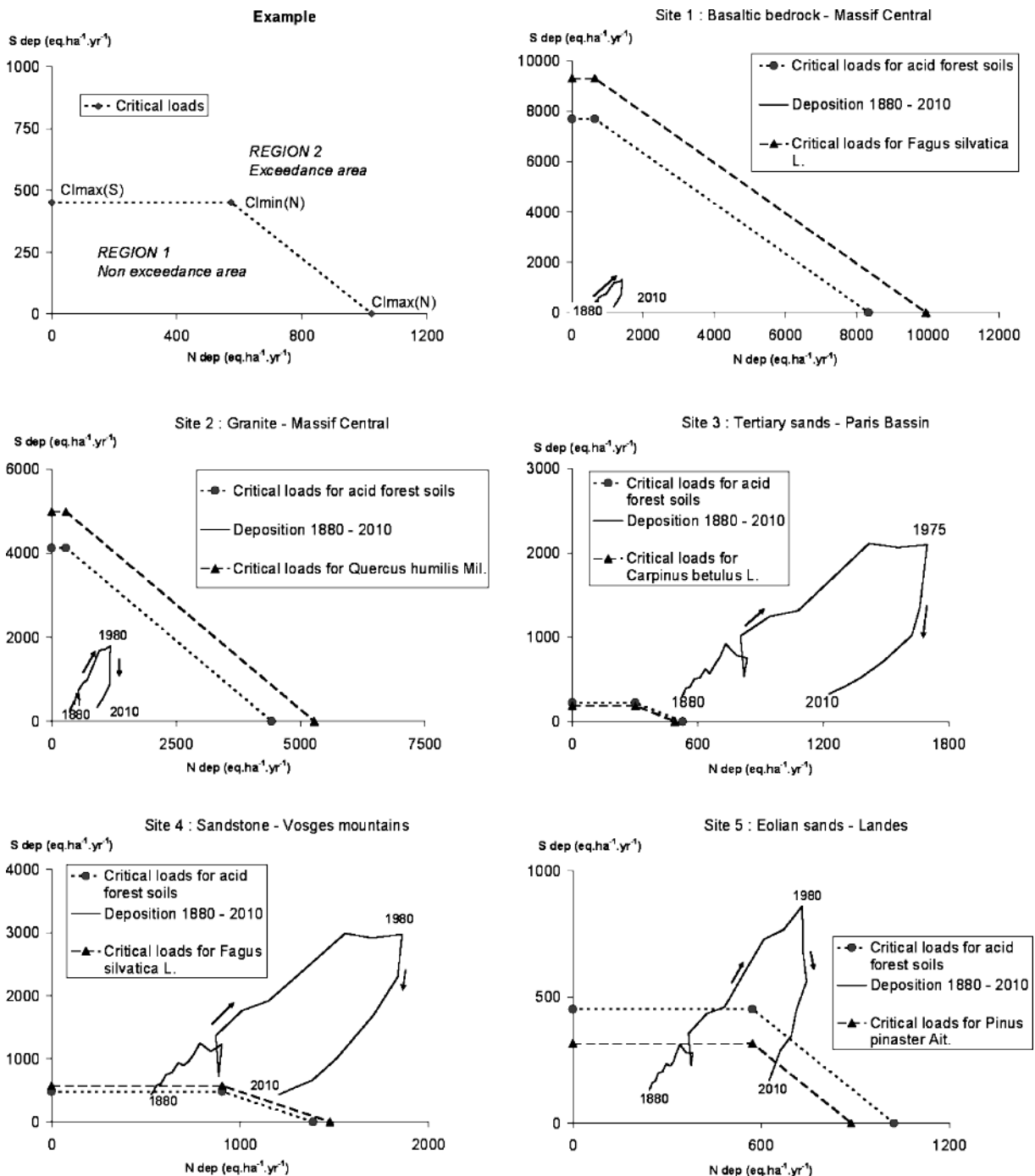


Fig. 1 Comparison between acid deposition (S, N) and two critical load functions for the acid forest soil ($\frac{[Al]}{[BC]} = 1.2$) and for the ecosystem indicator species

model integrated national emissions, stratospheric and atmospheric winds over Europe and meteorological data to determine the atmospheric deposition on a 150×150 km grid. Deposition data for S and N were

available under forest or vegetation cover. For the present study, historical deposition data for S and N over the 1880–2010 period was considered from EMEP deposition time-series (Schöpp, Posch, Mylona,

& Johansson, 2003). The deposition value over the 2010–2100 period was equal to the deposition negotiated in the Gothenburg protocol.

RENECOFOR present-day deposition data BC_{dep} (Ca, Na, K, Mg deposition), N_{dep} (NO_3 and NH_4 deposition), S_{dep} (sulfur deposition) and Cl_{dep} (Chloride deposition) were determined using field measurement data performed by the National Forest Office in charge of the RENECOFOR network for the period 1993–1996 and extrapolated to a 10×10 km grid (Croisé, Ulrich, Duplat, & Jaquet, 2005). Only open field deposition data were available at the national scale. To estimate the non-marine part of the deposition, all data have been sea-salt corrected considering Na deposition as 100% originating from sea-salts. The sea-salt ratio in sea-water was calculated from major ion concentrations in sea-water. To mitigate the lack of specialised

throughfall data at the national scale, a simple coefficient was applied to open field data to derive total deposition. This coefficient has been calculated on the RENECOFOR network sites and extrapolated to the ecosystem classification for critical load approach.

2.5.2 Soil Parameters

The physical and chemical soil data were determined from Brêthes and Ulrich (1997) and described in Table 2. The soils were pooled into three mineral layers. The layer thickness was the same for all the sites: 10 cm (layer 1), 30 cm (layer 2), 60 cm (layer 3). The CO_2 partial pressure in the three layers was set to 5, 10 and 20 times ambient partial pressure, respectively. The mineral surface area was calculated from

Table 2 Soil parameters and SAFE model input data for the five sites (1, 2, 3, 4 and 5) and the three soil layers

Site	1	2	3	4	5	Unit
Soil layers	0–10	0–10	0–10	0–10	0–10	cm
	10–40	10–40	10–40	10–40	10–40	
	40–100	40–100	40–100	40–100	40–100	
Bulk density	1,400	1,400	1,350	1,400	1,350	$kg\ m^{-3}$
	1,500	1,350	1,350	1,350	1,350	
	1,400	1,350	1,350	1,350	1,350	
Volumetric water content	0.1425	0.098	0.1	0.098	0.0675	$m^3\ m^{-3}$
	0.165	0.0675	0.0675	0.0675	0.0675	
	0.135	0.0678	0.04	0.0675	0.0675	
Mineral surf.	4.74	1.67	2.07	0.942	0.666	$10^6\ m^2\ m^{-3}$
	3.855	0.813	1.01	0.972	0.270	
	1.361	0.508	1.01	0.70	0.233	
CEC	12	8.72	1.74	2.88	3.65	$Ceq\ kg^{-1}$
	10	6.15	0.90	2.47	3	
	10	3.94	0.66	1.29	2.93	
Base sat. 1994	42	29	60	13	30	%
	68	14	17	4.9	27	
	94	11	47	6.2	18.3	
DOC	10	20	50	40	50	$mg\ l^{-1}$
	5	10	20	10	20	
	0	1.5	11	10	12	
Quartz	0	46.5	91.09	84.29	93.49	%
Olivine	20.91	0	0	0	0	
Orthose	7.80	22.7	3.87	9.28	3.15	
Plagioclases	59	17	2.80	0.80	2.72	
Apatite	2.36	0.29	0	0	0	
Biotite	0	13.51	1.92	4.23	0.53	
Muscovite	0	0	0	1	0	
Chlorite	9.93	0	0.32	0.40	0.11	

the soil texture and the bulk density of the soil according to Sverdrup and Warfvinge (1995).

2.5.3 Forest Nutrient Uptake and Management

For each ecosystem, the forest planting year has been set to 1800 with regular harvesting. Nutrient uptake values reached an equilibrium in 1980. For every ecosystem, it was assumed that 20% of the nutrient uptake was located in layer 1, 60% in layer 2 and 20% in layer 3. Values for nutrient uptakes have been shown in Table 2.

3 Results

3.1 Critical Loads and Exceedances

The comparison between acid deposition time-series (1880–2010) and critical loads of sulphur and nitrogen at the five sites, for two different critical limits, was depicted in Fig. 1. At site 1, the high critical loads were mainly due to the high weathering rate (2000 eq ha⁻¹ year⁻¹): the andosol was characterised by high content of fast dissolving minerals like olivine and apatite, and a particularly high content of plagioclase. At site 2, located on a granitic bedrock, the low weathering rate (250 eq ha⁻¹ year⁻¹) was due to slowly dissolving minerals and a relative high content of quartz. In the south of France, for both sites 1 and 2, a large part of the buffering capacity was due to high deposition of base cations, 1,011 and 1,507 eq ha⁻¹ year⁻¹, respectively (Moncoulon et al., 2004), mainly due to calcium inputs partly originating saharian dusts (Croisé et al., 2005). Acid deposition had never exceeded critical loads at sites 1 and 2 during the entire studied period. At site 3, both weathering rate (30 eq ha⁻¹ year⁻¹) and base cation deposition (210 eq ha⁻¹ year⁻¹) were low, explaining the low buffering capacity of this ecosystem. At this site, (S + N) deposition had exceeded critical loads during the entire studied period. At site 4, the podzol developed on sandstone presented a very low weathering rate due to high percent of quartz. However, probably originating the high pollution sources, base cation deposition was rather high (815 eq ha⁻¹ year⁻¹). This site was close to the German border, in the area where anthropogenic acid and basic deposition from Central Europe had been shown to be

important (Dambrine et al., 1995). At site 4, acid deposition had exceeded critical load since 1885 ($\frac{[Al]}{[BC]} = 1.2$) or 1890 ($\frac{[Al]}{[BC]} = 1.6$). At site 5, the weathering rate was very low (30 eq ha⁻¹ year⁻¹) on this acid sand podzol, whereas base cation atmospheric deposition (corrected from sea-salt influence) was intermediate (600 eq ha⁻¹ year⁻¹). On this site, the exceedance took place during 45 years ($\frac{[Al]}{[BC]} = 1.2$) or 60 years ($\frac{[Al]}{[BC]} = 0.85$).

3.2 Soil Solution Chemistry Modeling

Figure 2 depicted the pH estimated by SAFE over the 1900–2100 period at the five sites for the three soil layers. Acid deposition increased in the period 1950–1980 and decreased in the period 1980–2010. Thus, SAFE simulations were expected to show that soil solution pH decreased during the acidification period (1950–1980) and increased after 1980. After 2010, acid deposition was supposed to be constant and soil solution pH reached a new steady state.

At site 1, the effect of acid deposition during the 1950–1980 period was only significant in the first layer and pH remained constant after 1980. No significant variation occurred for $\frac{[Al]}{[BC]}$ ratio during the same period. At site 2, contrary to site 1, the pH of the second and third layers decreased during the 1950–1980 period, and the decrease continued until 2100. For these layers, the $\frac{[Al]}{[BC]}$ ratio had decreased between 1930 and 1950 and remained close to zero until nowadays. At site 3, the pH varied as expected in response to the acid deposition scenario for the whole soil profile. The $\frac{[Al]}{[BC]}$ ratio was higher than the critical limit for acid forest soils ($\frac{[Al]}{[BC]} = 1.2$) and for *Carpinus betulus* L. specifically ($\frac{[Al]}{[BC]} = 0.85$) in the three layers, all along the simulation. For the *Quercus* genus ($\frac{[Al]}{[BC]} = 1.6$), the Al/BC ratio was higher than the critical limit since 1900 (layer 1), 1940 (layer 2) and 1950 (layer 3), respectively with a time lag of 10, 50 and 60 years after critical load exceedance. At site 4, the pH varied as expected in response to the acid deposition scenario for the whole soil profile. The $\frac{[Al]}{[BC]}$ ratio reached the critical limit with a time lag of 30 years ($\frac{[Al]}{[BC]} = 1.2$) for the acid forest soil and 60 years ($\frac{[Al]}{[BC]} = 1.6$) for *Fagus sylvatica* L. in the topsoil layer. In the deeper soil, the time lag is 75 years (layer 2) and 80 years (layer 3) for both critical limits. Recovery was only simulated for *F. sylvatica* L. ($\frac{[Al]}{[BC]} = 1.6$) respectively in 2020 (layer 2)

and 2030 (layer 3). At site 5, the solution pH in the third layer kept on decreasing until today. Using the acid forest soil indicator ($\frac{[Al]}{[BC]} = 1.2$), the $\frac{[Al]}{[BC]}$ was higher than critical limit with a time lag of 10 years after exceedance of the critical load. In 2000, acid deposition reached a safe level (below critical load) in the first layer, and $\frac{[Al]}{[BC]}$ recovery occurred with a 10 years time delay.

4 Discussion and Conclusion

Among the five studied sites, only sites 1 and 2, both located in the Massif Central, have never been threatened by acid deposition. This is the result of both high critical loads – due to high weathering rates (site 1) and base cation deposition (site 1 and 2) – and remoteness from pollution sources. The three other

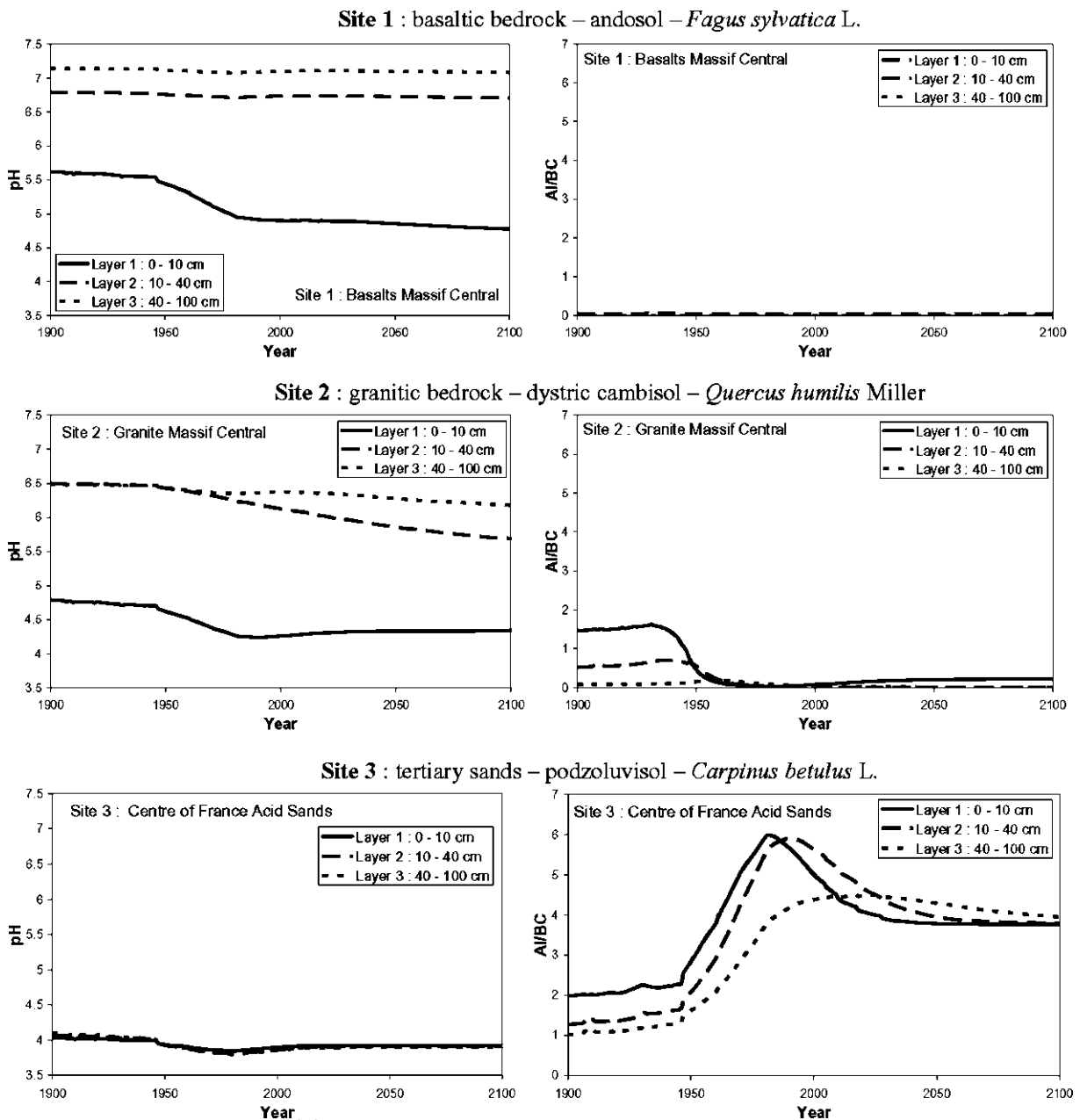
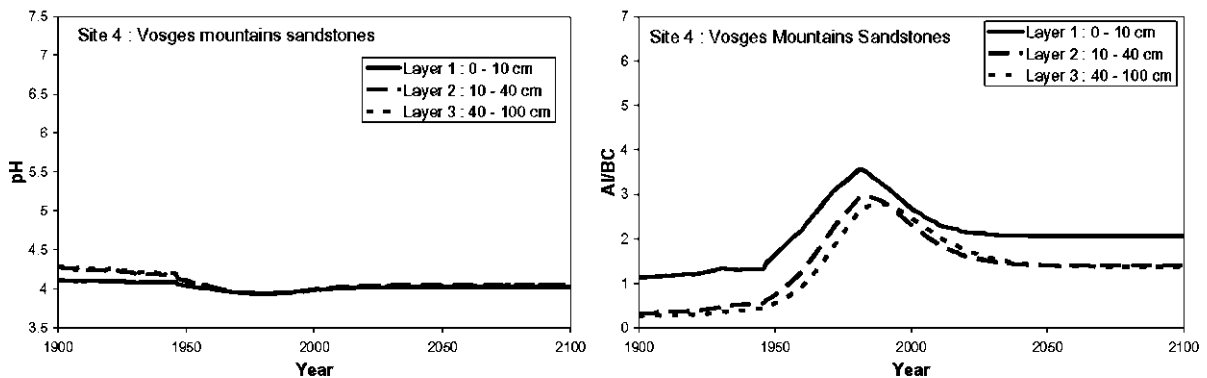


Fig. 2 Temporal trends of pH and $\frac{[Al]}{[BC]}$ ratio estimated by the SAFE model for the five studied sites

Site 4 : Sandstone – Podzol – *Fagus sylvatica* L.



Site 5 : Eolian sands – Podzol – *Pinus pinaster* Aiton

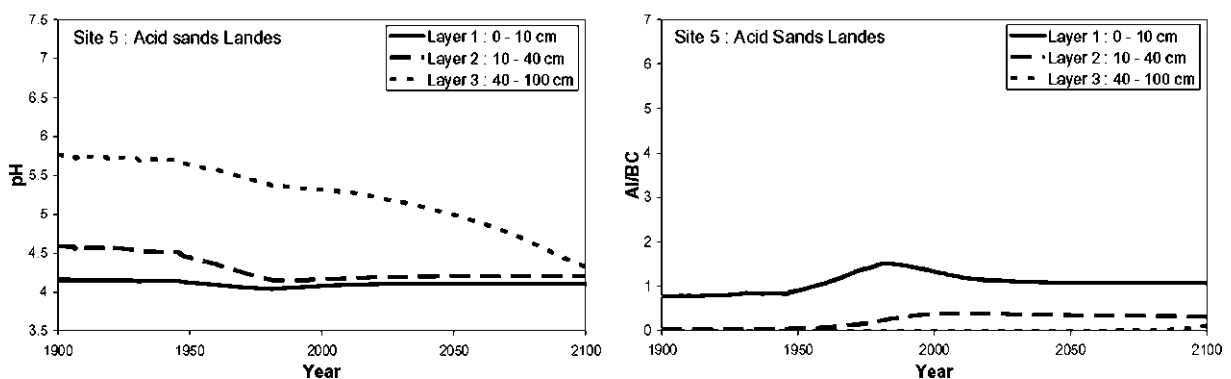


Fig. 2 (Continued)

sites were all submitted to critical load exceedances during different periods. At the Gothenburg protocol year, 2010, only site 5 will reach a non-exceedance state. Site 3 (Center of France) and site 4 (Vosges Mountains) will still be exceeded in 2010, mainly because of slow regressing nitrogen deposition.

Focusing on soil solution pH, the acidification of the top soil layer was significant at the five sites, even if these sites were not concerned by critical load exceedances. The acidification of the deeper layers was specifically detected at the most sensitive sites (3, 4) during the 1950–1980 period. Despite the acid deposition decrease, the high weathering rate at site 1 efficiently buffered the impact of acid inputs in the deeper soil. The acidification process in the deep layers was still running with a time lag at sites 2 and 5. This time delay in the deeper horizons indicated that, in sites 2 and 5, acidification has moved down the soil profile as a consequence of slow base cation depletion from CEC. Indeed, for site 2, base saturation decreased from 20 to 5% (second layer) between 1950 and 2050 and 11 to 6% (third layer) between 1980 and 2075.

For site 5, in the third layer, base saturation decreased from 25 to 1% between 1965 and 2100. This time lag in the deep horizons of sites 2 and 5, which were characterised by low weathering rates, was probably linked to the ratio of low acid inputs over a significant base cation atmospheric inputs. This guaranteed an efficient buffering capacity to the acidification of the soil profile. These behaviours in the deeper soil layers are not so surprising. Indeed, springwater analysis over the 1963–1996 period in the French Vosges mountains sandstones have shown a continuous acidification (Probst et al., 1999) whereas the sulphur deposition showed a 70% decrease by 1980.

The $\frac{[Al]}{[BC]}$ criterion was less sensitive than pH. During the acidification process, base cations were efficiently released from the humic and clay complex by protons exchange and $\frac{[Al]}{[BC]}$ ratio did not change significantly or even decreased in soils with high CEC (sites 1 and 2). In the andosol (site 1) and the dystric cambisol (site 2), the important base cation release from the exchangeable complex – reloaded mainly by weathering (site 1)

or atmospheric deposition (sites 1 and 2) – was the main process, which neutralised acid ions. On the opposite, because of the combination of poor base cation pool in the soil and high acid deposition, the acidification even concerned the deep soil of sites 3 and 4. The site 5, which was also very sensitive to acidification, received less acid deposition than sites 3 and 4, and thus $\frac{[Al]}{[BC]}$ ratio only exceeded the critical limit in the first layer. For site 5, recovery occurred in the first soil layer, 10 years after the end of critical load exceedance, thanks to significant base cation atmospheric deposition. This study presented a first estimation of the time delay between critical load and critical limit exceedance, using $\frac{[Al]}{[BC]}$ ratio: 10 to 30 years in the first soil layer and 50 to 90 years in the deepest soil. Comparison was made between the different values of critical $\frac{[Al]}{[BC]}$ for the different indicator species. The global acid forest soil indicator ($\frac{[Al]}{[BC]} = 1.2$) was an average value used for critical load calculations at the national scale. Regarding more precisely the different species, it appeared that the most acidification sensitive species, *Carpinus betulus*, was threatened, on site 3, 40 to 50 years before *Quercus* in the deepest soil layers. On site 4, *P. abies* was threatened 35 years before *F. silvatica* in the first soil layer and 5 to 10 years in the deepest soil.

In the present study, constant base cation deposition had been used, due to the lack of available time-series over the period. This was realistic on sites where natural base cation deposition was important (sites 1, 2 and 5) or on site 3 with poor base cation deposition. However, on site 4 (Vosges mountains), an important part of base cation deposition originated industrial emissions and was thus probably not constant over the period (Probst, Fritz, & Viville, 1995). As a consequence, such time-series would be used in the future to improve modelling results.

The sulphur and nitrogen deposition over the period 2010–2100 considered in the present study, corresponded to the Gothenburg protocol values. As we could observe on Fig. 1, the Gothenburg protocol deposition in 2100 will still exceed critical loads for sites 3 and 4. This was confirmed by the simulation of the soil solution response: no recovery for $\frac{[Al]}{[BC]}$ will occur without further deposition reduction. Moreover, acidification process was still detectable in sites 2 and 5. Even though significant sulphur deposition reduction after 1980 had reached its critical load in 4 sites on 5, further reduction of nitrogen will be needed to

reach a safety situation in sensitive ecosystems. Moreover, this study highlighted the importance of taking into account not only weathering rates and vegetation uptake but also the relative ratio between base cation deposition and acid compounds to predict ecosystem response to atmospheric pollution scenario.

Acknowledgements The authors are grateful to Jean-Paul Hettelingh and an anonymous reviewer for their fruitful comments, and thank the ADEME, particularly Laurence Galsomiers, for supporting the French NFC investigations. The authors also thank Erwin Ulrich for providing RENECOFOR data and Jean-Paul Party for his appreciated expertise.

References

- Alveteg, M., Walse, C., & Warfvinge, P. (1998). Reconstructing historical atmospheric deposition and nutrient uptake from present day value using MAKEDEP. *Water, Air and Soil Pollution*, 104(3–4), 269–283.
- Blank, L. W. (1985). A new type of forest decline in Germany. *Nature*, 314, 311–314.
- Brêthes, A., & Ulrich, E. (1997). RENECOFOR – Caractéristiques pédologiques des 102 peuplements du réseau. Office National des Forêts (Eds.), p. 573.
- Citepa (2003). Emissions dans l'air en France. Métropole. Substances impliquées dans les phénomènes d'acidification, d'eutrophisation et de photochimie. <http://www.citepa.org/pollution/index.htm>.
- Croisé, L., Ulrich, E., Duplat, P., & Jaquet, O. (2005). Two independent methods for mapping bulk deposition in France. *Atmospheric Environment*, 39(21), 3923–3941.
- Dambrine, E., Ulrich, E., Cenac, P., Durand, P., Gauquelin, T., Mirabel, P., et al. (1995). Atmospheric deposition in France and possible relation to forest decline. In G. Landmann & M. Bonneau M. (Eds.), *Forest decline and atmospheric deposition effects in the French mountains* (pp. 177–199). Berlin, Heidelberg, New York: Springer, 461.
- Hettelingh, J. P., Posch, M., & De Smet, P. A. M. (2001). Multi-effect critical loads used in multi-pollutant reduction agreements in Europe. *Water Air and Soil Pollution*, 130, 1133–1138.
- Iversen, T. (1993). Modelled and measured transboundary acidifying pollution in Europe – Verification and trends. *Atmospheric Environment*, 27A, 889–920.
- Landmann, G. & Bonneau, M. (Eds.) (1995). Forest decline and atmospheric deposition effects in the French mountains.
- Moncoulon, D., Probst, A., & Party, J. P. (2004). Critical loads of acidity: Importance of weathering, atmospheric deposition and vegetation uptake for ecosystem sensitivity determination. *C.R. Geoscience*, 336, 1417–1426.
- Nilsson, J., & Grennfelt, P. (1988). *Critical loads for nitrogen and sulphur. Miljørapport 11*. Copenhagen: Nordic Council of Ministers.
- Party (1999). Acidification des sols et des eaux de surface des écosystèmes forestiers français: facteurs, mécanismes et tendances. Taux d'altération sur petits bassins versants silicatés. Application au calcul des charges critiques

- d'acidité., thèse de l'Université Louis Pasteur de Strasbourg, 247p.
- Probst, A., Fritz, B., & Viville, D. (1995). Mid-term trends in acid precipitation, streamwater chemistry and element budgets in the Strenbach catchment (Vosges mountains, France). *Water, Air and Soil Pollution*, 79, 39–59.
- Probst, A., Massabuau, J. C., Probst, J. L., & Fritz, B. (1990). Acidification des eaux de surface sous l'influence des précipitations acides : rôle de la végétation et du substratum, conséquences pour les populations de truites. Le cas des ruisseaux des Vosges. *C.R. Acad. Sci. Paris*, 311, 405–411.
- Probst, A., Party, J. P., Fevrier, C., Dambrine, E., Thomas, A. L., & Stussi, J. M. (1999). Evidence of springwater acidification in the Vosges mountains (north-east of France): Influence of bedrock buffering capacity. *Water, Air and Soil Pollution*, 114, 395–411.
- Schöpp, W., Posch, M., Mylona, S., & Johansson, M. (2003). Long term development of acid deposition (1880–2030) in sensitive freshwater regions in Europe. *Hydrology and Earth Science Systems*, 7, 436–446.
- Sverdrup, & Warfvinge (1993). The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. Reports in ecology and environmental engineering, Lund University, Department of Chemical Engineering II.
- Sverdrup, H., & Warfvinge, P. (1995). Estimating field weathering rates using laboratory kinetics. *Reviews in Mineralogy*, 31, 485–541.
- Uba (2004). Manual on methodologies and criteria for Modeling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends. UN-ECE Convention on Long Range Transboundary Air Pollution, Federal Environmental Agency (Umweltbundesamt), Berlin.
- Warfvinge, P., Falkengren-Grerup, U., & Sverdrup, H. (1993). Modelling long-term base cation supply to acidified forest stands. *Environmental Pollution*, 80, 209–220.
- Wright, R. F., & Snekvik, E. (1978). Acid precipitation: Chemistry and fish population in 700 lakes in southernmost Norway. *Verhandlung der Internationalen Vereinigung für Theoretische und Angewandte Limnologie*, 20, 765–775.

Recovery of Acidified Lakes: Lessons From Sudbury, Ontario, Canada

W. Keller · N. D. Yan · J. M. Gunn · J. Heneberry

Received: 13 June 2005 / Accepted: 3 April 2006 / Published online: 6 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Over 7,000 lakes around Sudbury, Ontario, Canada were acidified by S deposition associated with emissions from the Sudbury metal smelters and more distant S sources. Air pollution controls have led to widespread changes in damaged Sudbury lakes, including increased pH and decreased concentrations of SO₄, metals and base cations. While chemical improvements have often been substantial, many lakes are still acidified, although water quality recovery is continuing. Biological recovery has been observed in some lakes among various groups of organisms including fish, zooplankton, phytoplankton and zoobenthos. Generally, however, biological recovery is still at an early stage. Lakes around Sudbury are also showing that the recovery of acid-damaged lakes is closely linked to the effects of other major environmental stressors such as climate change, base

cation depletion and UV-B irradiance. Future studies of the recovery of acid-damaged lakes around Sudbury, and in other regions, will need to consider the interactions of these and other stressors.

Keywords acidification · lakes · recovery · Sudbury · sulphur · stressors · interaction

1 Introduction

Metal mining and smelting began in the Sudbury, Ontario, Canada, area before the turn of the twentieth century, and the area grew into one of the largest metal-producing complexes in the world. Smelter emissions peaked during the 1960s, when the Sudbury area smelters constituted one of the world's largest point sources of SO₂ emissions. Thousands of tons of metal particulates have also been emitted from the Sudbury smelters over the years. Lakes in a large area of northeastern Ontario were severely affected by the atmospheric deposition of contaminants originating from the Sudbury smelter emissions. Over 7,000 lakes within a 17,000 km² area (Fig. 1) were acidified to pH < 6.0, the point at which significant biological damage is expected (Neary, Dillon, Munro, & Clark, 1990). The lakes most severely damaged were those located within about 20–30 km of the smelters, where acid conditions were combined with very high concentrations of potentially toxic trace metals, especially Cu and Ni.

W. Keller · J. M. Gunn · J. Heneberry
Cooperative Freshwater Ecology Unit,
Laurentian University,
Sudbury P3E 2C6 ON, Canada

W. Keller (✉) · J. Heneberry
Ontario Ministry of the Environment,
Biomonitoring Section,
Sudbury, Canada
e-mail: bkeller@vianet.ca

N. D. Yan
Biology Department, York University,
4700 Keele Street,
Toronto, ON M3J 1P3, Canada

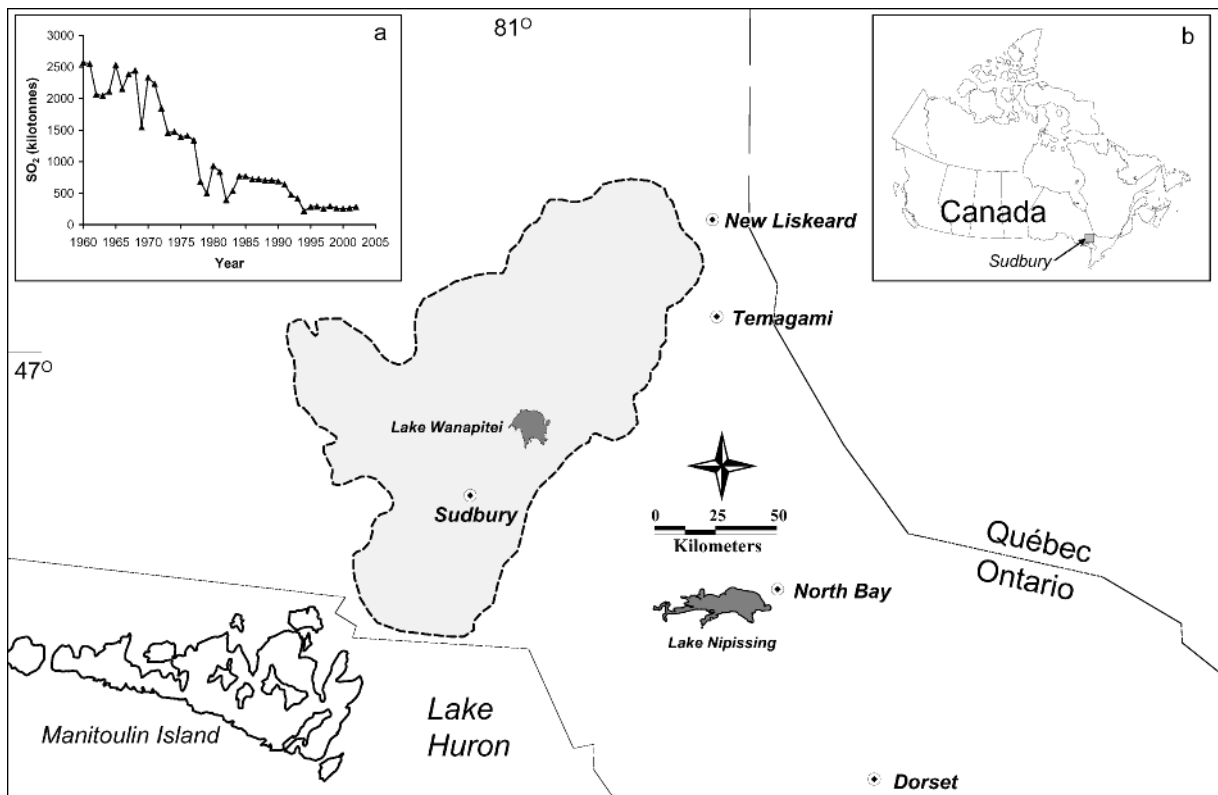


Fig. 1 The 17,000 km² zone of effect on lakes around Sudbury (*Inset a*, SO₂ emissions from the Sudbury area smelters; *Inset b*, the location of Sudbury, Ontario, Canada)

However, much has changed in the aquatic ecosystems around Sudbury. As emissions of SO₂ and metals were dramatically reduced during the 1970s (Fig. 1), large improvements in lake water quality were observed in the surrounding area (Keller & Pitblado, 1986; Keller, Pitblado, & Carbone, 1992) and biological improvements began to follow (Gunn & Keller, 1990; Havas et al., 1995; Keller & Yan, 1991). Large additional decreases in SO₂ emissions were achieved by 1994 (Fig. 1). Overall, reductions in SO₂ and metal emissions of about 90% have been achieved in recent decades. This paper presents long-term trends in the chemistry of Sudbury lakes and examines the physical, chemical and biological factors that may influence lake recovery processes.

2 Changes in Lake Chemistry

Large changes in lake chemistry followed the reductions of SO₂ emissions that occurred during the 1970s, including increased pH and alkalinity and decreased

concentrations of SO₄, base cations and metals (Gunn & Keller, 1990; Keller, Dillon, Heneberry, Malette, & Gunn, 2001b; Keller, Dixit, & Heneberry, 2001a; Keller, Heneberry, & Dixit, 2003; Keller, Heneberry, & Gunn, 1999a; Keller & Pitblado, 1986; Keller et al., 1992). Changes continued in the 1990s, during which additional pollution controls were implemented at the Sudbury smelters. Sulphate concentrations declined greatly during this period, following substantial declines in earlier years (Keller & Pitblado, 1986). The strong relationship between SO₄ and distance from Sudbury observed in previous surveys (Keller & Pitblado, 1986) had become much weaker by 2004 (Fig. 2), and most Sudbury area lakes now have SO₄ concentrations similar to reference lakes near Dorset, ~200 km to the southeast.

In response to reduced S deposition, substantial increases in the pH of acidified Sudbury lakes have been observed. In a set of 44 acidic lakes monitored since 1981, the number of highly acidic lakes (pH < 5.0) declined from 28 to 6 by 2004 (Fig. 3). None of this set of study lakes were non-acidic in 1981; by

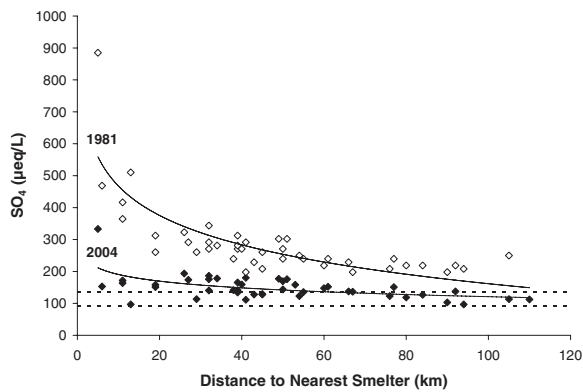


Fig. 2 Sulphate concentrations in lakes as a function of distance from Sudbury smelters in 1981 and 2004. The range of recent (1998–2001) SO_4 concentrations in 42 lakes near Dorset, ~200 km southeast of Sudbury, is indicated by the dashed horizontal lines

2004, 14 of the lakes had $\text{pH} > 6.0$, a level sufficient for protection of most acid-sensitive aquatic biota (Neary et al., 1990). Decreases in SO_4 concentrations have, however, been partially balanced by decreases in base cation concentrations as well as decreased acidity. Examples of the temporal changes in SO_4 , Ca and pH in one key long-term monitoring lake are shown in Fig. 4.

Substantial declines in concentrations of metals originating from the smelters (eg. Cu, Ni) and from acid-leaching of watersheds (eg. Al, Mn) have also occurred in Sudbury lakes. Concentrations of smelter-related metals, such as Ni, are now only substantially elevated in lakes within about 20–30 km of the Sudbury smelters (Keller et al., 1999a). Concentrations of metals related to watershed acidification,

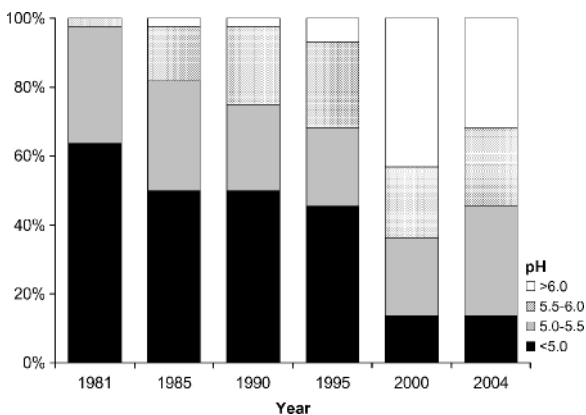


Fig. 3 Distribution of pH in 44 Sudbury lakes in surveys conducted between 1981 and 2004

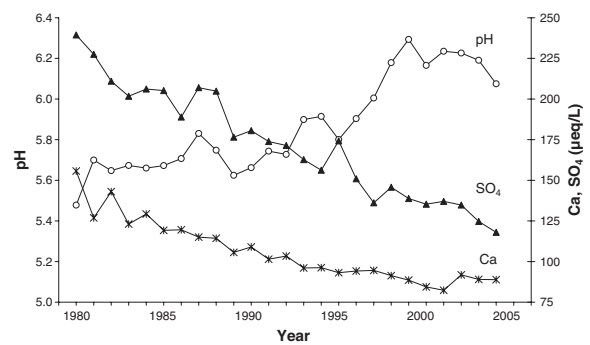


Fig. 4 Long-term changes in pH, SO_4 and Ca in Whitepine Lake, 89 km north of Sudbury

particularly Al, are still elevated in some lakes, notably the lakes that are still most acidic (pH vs. total Al: $r = 0.77$, $p < 0.05$; 44 lakes sampled in 2004; range in total Al 12–386 $\mu\text{g/l}$).

While dramatic changes in lake chemistry have accompanied emission reductions, temporal patterns in lake chemistry cannot simply be attributed to the direct effects of pollution controls. Weather patterns have a profound effect on long term patterns in lake chemistry (Schindler, Curtis, Parker, & Stainton, 1996), as has been observed in the Sudbury area (Keller et al., 1992). Drought can lead to oxidation of stored S in lake catchments. When wet conditions resume, the release of this stored acidity can lead to lake re-acidification and many related physical and chemical changes including metal mobilization, changes in thermal structure, and increased UV-B penetration (Yan, Keller, Scully, Lean, & Dillon, 1996a). Such effects were observed in Sudbury area lakes following the 2-year drought of 1986–87 (Keller et al., 1992; Yan et al., 1996a) and had large impacts on zooplankton and phytoplankton communities in Swan Lake (Arnott, Yan, Keller, & Nicholls, 2001). Some of the recent changes in the chemistry of Sudbury lakes may still reflect recovery from this drought-induced acidification event. Recent changes may also, in part, still be a continuation of the general long-term recovery of lakes and watersheds that began decades ago in the Sudbury area.

3 Biological Recovery

Lakes in the large zone affected by the Sudbury smelter emissions are showing substantial evidence of biological recovery (Findlay, 2003; Holt & Yan,

2003; Keller, Gunn, & Yan, 1999b; Keller & Yan, 1998; Keller, Yan, Somers, & Heneberry, 2002; Snucins, 2003). Populations of a number of acid and/or metal-sensitive invertebrate species, including many common crustacean zooplankters such as *Daphnia mendotae*, *Skistodiaptomus oregonensis*, *Epischura lacustris*, and *Eubosmina longispina* have been observed to recolonize some lakes (Keller & Yan, 1991; Keller et al., 2002; Yan, Keller, Somers, Pawson, & Girard, 1996b). While zooplankton communities in some lakes have shown recovery, in most cases they are not yet completely similar to communities in non-acidic reference lakes (Keller et al., 2002; Yan et al., 2004; Yan et al., 1996b). Copepods appear to have recovered to a greater degree than cladocerans (Yan et al., 2004). Colonization by acid-sensitive benthic invertebrates, including amphipods and mayflies has also been observed in recovering lakes (Snucins, 2003).

The phytoplankton community of Clearwater Lake, one of the most highly affected Sudbury lakes in the 1970s, has now become similar to communities of near-neutral, more pristine lakes on the Precambrian Shield (J. Winter, unpublished manuscript). Evidence of recovery of phytoplankton communities has also been observed in other Sudbury area lakes (Findlay, 2003; Nicholls, Nakamoto, & Keller, 1992). Increased diversity and a shift away from dominance by dinoflagellates to increased importance of acid-sensitive chrysophytes has been a common pattern during the recovery of phytoplankton communities.

The process of biological recovery from acidification is very complex (Keller et al., 1999b; Keller & Yan, 1998; Yan et al., 2003). It involves the interplay of biological, chemical, and physical factors that control the arrival and success of colonists (Fig. 5). The rate and extent of biological recovery in Sudbury lakes appear to be related to both the initial severity of damage and continuing habitat limitations. Invertebrate community recovery in severely affected Sudbury lakes, even lakes that have maintained near-neutral conditions for many years, is still limited. Elevated lakewater concentrations of metals, and metal-contaminated sediments, undoubtedly still affect aquatic communities in some lakes close to the Sudbury smelters. For example, within ~20 km of Sudbury, concentrations of Cu and Ni often greatly exceed Ontario government water quality objectives for protection of aquatic life (5 and 25 µg/l, respectively),

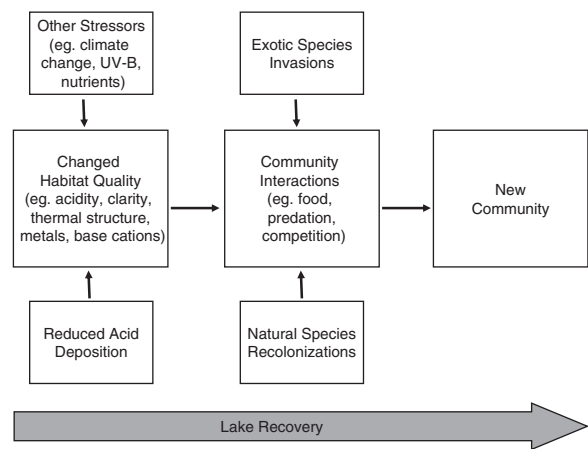


Fig. 5 Relationships between some factors influencing the recovery of lakes from acidification

and severe effects guidelines for sediments (110 and 75 µg/g, respectively).

Nickel, in particular, has been implicated as the contaminant most responsible for sediment toxicity to the amphipod *Hyaella* in lakes within the City of Sudbury (Borgmann, 2003). Elevated waterborne metal concentrations are a likely explanation for the lack of recovery of cladoceran zooplankton in Middle Lake, in Sudbury (Yan et al., 2004). In Middle Lake (Yan et al., 2004) and in Whitepine Lake (Keller et al., 2002) a number of new zooplankton species appeared sporadically, but did not become successfully established, suggesting that habitats had not sufficiently recovered at the time of invasion. These included *D. mendotae*, *Daphnia retrocurva*, and *S. oregonensis*, in Whitepine Lake and *Holopedium gibberum*, *Daphnia dubia*, *Daphnia longiremis*, *Daphnia pulex*, *D. retrocurva* and *Eubosmina tubicen* in Middle Lake.

Biological as well as chemical factors may have a large influence on the recovery of aquatic communities from acidification. For example, in cases where the elimination of fish has resulted in zooplankton communities controlled by invertebrate predators, zooplankton communities are not likely to recover without the re-establishment of planktivorous fish populations (Keller et al., 2002). Fish are also expected to have direct effects on community recovery as residual fish populations expand and new fish species become established through natural invasions, or through intentional or unintentional introductions. In particular, the ongoing northward expansion of

smallmouth bass (*Micropterus dolomieu*) populations in Ontario, which will likely be enhanced under a warming climate, has large implications for aquatic systems (Vander Zanden, Wilson, Casselman, & Yan, 2004) and hence for the recovery of aquatic communities in Sudbury area lakes. Smallmouth bass are important predators on planktivorous fish, which in turn affect planktonic food webs. The simple fish communities occurring early in the recovery of some Sudbury lakes are often dominated by large populations of stunted yellow perch (*Perca flavescens*). Heavy predation by perch may be a factor inhibiting the recovery of cladoceran zooplankton communities (Yan et al., 2004).

The dispersal of species is also an important part of the recovery process. However, the eventual appearance of many common crustacean zooplankton species in long-term lake records (Keller & Yan, 1991; Keller et al., 2002; Yan et al., 2004; Yan et al., 1996b) suggests that dispersal will not be a major control on zooplankton recovery in the long term. Dispersal will also probably ultimately depend largely on time for many other invertebrates. With enough time many invertebrate species can reasonably be expected to naturally colonize recovering Sudbury lakes. This expectation is supported by a number of examples of effective dispersal by zooplankton, phytoplankton and benthic invertebrate species to lakes in the Sudbury area that did not have residual populations (Pollard, Colbourne, & Keller, 2003; Watson, Hunt, & Keller, 1999).

4 Factors Complicating Lake Recovery

The effects of large-scale stressors including climate change, UV-B irradiance, and acidification are linked (Yan et al., 1996a), and these and other ecosystem interactions will affect lake recovery processes (Fig. 5). Biological recovery will be affected not just by lake chemistry, but by the sometimes dramatic physical changes such as altered transparency and thermal regimes that accompany chemical recovery. Drought-induced re-acidification episodes may set back biological recovery (Arnott et al., 2001). Effects of climate change may interact with changes in acidity and resultant changes in lake clarity to affect lake thermal structure (Keller, Heneberry, & Leduc, 2005; Yan et al., 1996a). As well, expansions of some

non-indigenous species may be promoted by climate change with resultant effects on recovering aquatic communities (Vander Zanden et al., 2004). Calcium declines could alter distributions of some Ca-rich biota, and increase the sensitivity of some organisms to acid, metals or UV-B (Keller et al., 2001a). These are just some of the ways that the recovery of lakes from acidification may be affected by stressor interactions. Future studies of lake recovery will need to be done within a multiple stressor framework.

5 Conclusions

Lakes in the Sudbury area provide one of the best examples in the world of the environmental benefits of SO₂ emission controls. However, despite dramatic water quality improvements, some Sudbury lakes are still acidic and metal-contaminated. Much evidence of biological recovery is emerging for many groups of aquatic biota including zooplankton, phytoplankton, benthic invertebrates and fish. However, severely damaged biological communities have often been slow to recover, in part reflecting continuing habitat quality limitations. Future recovery of Sudbury lakes from acidification and metal contamination will also be influenced by the effects of other regional (eg. arrival of invasive species) and global (eg. climate change) factors.

Acknowledgements This paper is a contribution from the Aquatic Restoration Group of the Cooperative Freshwater Ecology Unit, a partnership between Laurentian University, the Ontario Ministry of the Environment, the Ontario Ministry of Natural Resources, CVRD Inco (formerly Inco Ltd.), Xstrata Nickel (formerly Falconbridge Ltd.), and Environment Canada.

References

- Arnott, S. E., Yan, N., Keller, W., & Nicholls, K. (2001). The influence of drought-induced acidification on the recovery of plankton in Swan Lake (Canada). *Ecological Applications*, 11, 747–763.
- Borgmann, U. (2003). Derivation of cause-effect based sediment quality guidelines. *Canadian Journal of Fisheries and Aquatic Sciences*, 60, 352–360.
- Findlay, D. L. (2003). Response of phytoplankton communities to acidification and recovery in Killarney Park and the Experimental Lakes Area, Ontario. *Ambio*, 32, 190–195.
- Gunn, J. M., & Keller, W. (1990). Biological recovery of an acid lake after reductions in industrial emissions of sulphur. *Nature*, 345, 431–433.

- Havas, M., Woodfine, D. G., Lutz, P., Yung, K., MacIsaac, H. J., & Hutchinson, T. C. (1995). Biological recovery of two previously acidified, metal-contaminated lakes near Sudbury, Ontario, Canada. *Water, Air and Soil Pollution*, 85, 791–796.
- Holt, C., & Yan, N. D. (2003). Recovery of crustacean zooplankton communities from acidification in Killarney Park, Ontario, 1971–2000: pH 6 as a recovery goal. *Ambio*, 32, 203–207.
- Keller, W., Dillon, P. J., Heneberry, J., Malette, M., & Gunn, J. M. (2001b). Sulphate in Sudbury, Ontario, Canada lakes: Recent trends and status. *Water, Air, and Soil Pollution*, 130, 793–798.
- Keller, W., Dixit, S. S., & Heneberry, J. (2001a). Calcium declines in northeastern Ontario lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 58, 2011–2020.
- Keller, W., Gunn, J. M., & Yan, N. D. (1999b). Acid rain – perspectives on lake recovery. *Journal of Aquatic Ecosystem Stress and Recovery*, 6, 207–216.
- Keller, W., Heneberry, J. H., & Dixit, S. S. (2003). Decreased acid deposition and the chemical recovery of Killarney, Ontario, lakes. *Ambio*, 32, 183–189.
- Keller, W., Heneberry, J., & Gunn, J. M. (1999a). Effects of emission reductions from the Sudbury smelters on the recovery of acid and metal-damaged lakes. *Journal of Aquatic Ecosystem Stress and Recovery*, 6, 189–198.
- Keller, W., Heneberry, J. H., & Leduc, J. (2005). Linkages between weather, dissolved organic carbon, and cold-water habitat in a Boreal Shield lake recovering from acidification. *Canadian Journal of Fisheries and Aquatic Sciences*, 62, 340–346.
- Keller, W., & Pitblado, J. R. (1986). Water quality changes in Sudbury area lakes: A comparison of synoptic surveys in 1974–76 and 1981–83. *Water, Air, and Soil Pollution*, 29, 285–296.
- Keller, W., Pitblado, J. R., & Carbone, J. (1992). Chemical responses of acidic lakes in the Sudbury, Ontario, area to reduced smelter emissions, 1981–1989. *Canadian Journal of Fisheries and Aquatic Sciences*, 49(Suppl. 1), 25–32.
- Keller, W., & Yan, N. D. (1991). Recovery of crustacean zooplankton species richness in Sudbury area lakes following water quality improvements. *Canadian Journal of Fisheries and Aquatic Sciences*, 48, 1635–1644.
- Keller, W., & Yan, N. D. (1998). Biological recovery from lake acidification: Zooplankton communities as a model of patterns and processes. *Restoration Ecology*, 6, 364–375.
- Keller, W., Yan, N. D., Somers, K. M., & Heneberry, J. H. (2002). Crustacean zooplankton communities in lakes recovering from acidification. *Canadian Journal of Fisheries and Aquatic Sciences*, 59, 726–735.
- Neary, B. P., Dillon, P. J., Munro, J. R., & Clark, B. J. (1990). *The acidification of Ontario lakes: An assessment of their sensitivity and current status with respect to biological damage* (Tech. Rep., p. 171). Dorset, Ontario, Canada: Ontario Ministry of Environment.
- Nicholls, K. H., Nakamoto, L., & Keller, W. (1992). Phytoplankton of Sudbury area lakes (Ontario) and relationships with acidification status. *Canadian Journal of Fisheries and Aquatic Sciences*, 49(Suppl. 1), 40–51.
- Pollard, H. G., Colbourne, J. C., & Keller, W. (2003). Reconstruction of centuries-old *Daphnia* communities in a lake recovering from acidification and metal contamination. *Ambio*, 32, 214–218.
- Schindler, D. W., Curtis, P. J., Parker, B. R., & Stainton, M. P. (1996). Consequences of climate warming and lake acidification for UV-B penetration in North American boreal lakes. *Nature*, 379, 705–708.
- Snucins, E. (2003). Recolonization of acid damaged lakes by the benthic invertebrates *Stenacron interpunctatum*, *Stenonema femoratum*, and *Hyalella azteca*. *Ambio*, 32, 225–229.
- Vander Zanden, J., Wilson, K. A., Casselman, J. M., & Yan, N. D. (2004). Species introductions and their impacts in North American Shield lakes, Chapter 13. In J. M. Gunn, R. J. Steedman, & R. A. Ryder (Eds.), *Boreal shield watersheds – lake trout ecosystems in a changing environment*. Boca Raton: CRC.
- Watson, G., Hunt, C., & Keller, W. (1999). Natural and enhanced aquatic ecosystem development at Inco's former Garson 10.2 open pit mine, p. 419–428. In D. Goldsack, N. Belzile, P. Yearwood, & G. Hall (Eds.), *Proceedings mining and the environment II*. Sudbury, Ontario.
- Yan, N. D., Girard, R., Heneberry, J., Keller, W., Gunn, J., & Dillon, P. J. (2004). Recovery of copepod, but not cladoceran, zooplankton from severe and chronic effects of multiple stressors. *Ecology Letters*, 7, 452–460.
- Yan, N. D., Keller, W., Scully, N. M., Lean, D. R. S., & Dillon, P. J. (1996a). Increased UV-B penetration in a lake owing to drought-induced acidification. *Nature*, 382, 141–143.
- Yan, N. D., Keller, W., Somers, K. M., Pawson, T. W., & Girard, R. G. (1996b). Recovery of crustacean zooplankton communities from acid and metal contamination: Comparing manipulated and reference lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 53, 1301–1327.
- Yan, N. D., Leung, B., Keller, W., Arnott, S. E., Gunn, J. M., & Raddum, G. G. (2003). Developing conceptual frameworks for the recovery of aquatic biota from acidification. *Ambio*, 32, 165–169.

Relationships Between Macroinvertebrate Assemblages of Stony Littoral Habitats and Water Chemistry Variables Indicative of Acid-stress

Richard K. Johnson · Willem Goedkoop ·
Jens Fölster · Anders Wilander

Published online: 21 February 2007
© Springer Science + Business Media B.V. 2007

Abstract Gradient analyses were used to correlatively determine the importance of acid-related variables for littoral macroinvertebrate assemblages. To better ascertain the effects of acidity on macroinvertebrate assemblages we removed sites judged to be affected by other stressors such as agriculture, urbanization and liming. PCA of land use and water chemistry confirmed the presence of an acidity gradient; several acidity variables (e.g. pH and buffering capacity) were strongly correlated with the first PC axis, which explained Ca 32% of the variance in the environmental data. Partial constrained ordination of littoral macroinvertebrate assemblages with water chemistry, after removing the effect of other confounding variables (e.g. land use/type), showed that acidity variables accounted for significant amounts of among-lake variability in assemblage structure. Regression of canonical scores (a metric of community composition) and diversity with pH and alkalinity was used to visually determine ecological breakpoints or threshold values. Five classes were established for pH: $\text{pH} < 5$ (extremely acid), $5 < \text{pH} \leq 5.6$ (very acid),

$5.6 < \text{pH} \leq 6.2$ (acid), $6.2 < \text{pH} \leq 6.8$ (weakly acid) and $\text{pH} > 6.8$ (neutral-alkaline). Similarly, three classes were determined for alkalinity/acidity: < 0.02 , $0.02\text{--}0.1$ and > 0.1 meq/L.

Keywords acidity · biological response · littoral macroinvertebrates · lakes

1 Introduction

Acidification is still considered as a serious threat to the biodiversity and functioning of Swedish inland surface waters. In the early 1990s, it was estimated that some 14,000 or 15% of Swedish lakes with a surface area $< 1 \text{ km}^2$ and about one-fifth of all watercourses could be regarded as being adversely affected by acidification (Bernes, 1991). More recently, natural recovery of water chemistry has been documented in a number of lake ecosystems in Sweden (Wilander, 1997) and across Europe (Stoddard et al., 1999), and studies of Norwegian lakes have attributed recovery of lake biology to decreased deposition of acidifying compounds (e.g. Halvorsen, Heegaard, Fjellheim, & Raddum, 2003). By contrast, studies showing “natural” biological recovery of Swedish lakes are scarce (e.g. Stendera & Johnson, submitted).

Biological response variables are often selected over physical-chemical variables because they generally represent valued ecosystem attributes such as

R. K. Johnson (✉) · W. Goedkoop ·
J. Fölster · A. Wilander
Department of Environmental Assessment,
Swedish University of Agricultural Sciences,
Box 7050, SE 750 07 Uppsala, Sweden
e-mail: Richard.Johnson@ma.slu.se

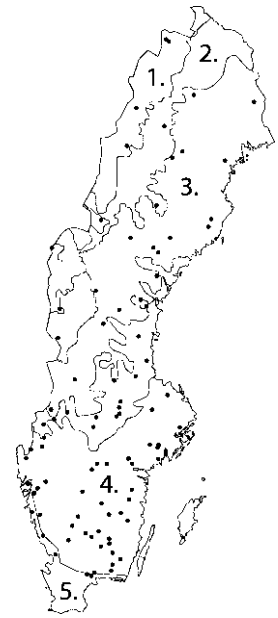
species richness or ecosystem productivity. The use of biological variables in monitoring programs is, however, not always justifiable for logistic and/or economic reasons. For example, the large number of lakes in Sweden (e.g. >100,000) prohibits the sole use of biological variables in national, and to some extent even regional, monitoring programs due to the high costs associated with sampling and processing. Hence, chemical monitoring is relatively widespread. Clearly, if physico-chemical variables are to be used as surrogates for biological variables, then knowledge of stress-response relationships are needed for devising reliable models. This study was designed to correlatively assess relationships between littoral benthic macroinvertebrate communities and physico-chemical variables indicative of acid stress. In particular, we were interested in determining which physico-chemical variables are best correlated with changes in littoral macroinvertebrate composition. Building then on this information of “stress-response” relationships we analyzed the data from a lake acidification gradient to determine if biological threshold(s) could be determined between selected physico-chemical and biological variables.

2 Material and Methods

2.1 Study Lakes

Approximately 126 lakes are monitored annually for surface water chemistry and biology as part of the national lake monitoring program (<http://www.ma.slu.se>). To more unequivocally analyze the effects of acidity on macroinvertebrate communities, we removed lakes judged to be affected by other anthropogenic stressors such as agriculture (e.g. total phosphorus concentration > expected background levels or >20% of the catchment classified as agriculture), urbanization (>0.1% of the catchment classified as urban), and liming. Hence, the data set used here ($n=90$) consisted of reference lakes and lakes deemed to be affected by acidification (Fig. 1). The lakes have, on average, been monitored for water chemistry and littoral macroinvertebrates for nine years; minimum study period was one year ($n=8$ lakes) and the maximum study period was 16 years ($n=12$ lakes). The majority of lakes were located in the mixed forest ecoregion in the south

Fig. 1 Location of the 90 reference and acid-stressed lakes by six ecoregions. 1=arctic/alpine, 2=northern boreal, 3=middle boreal, 4=southern boreal, 5=boreonemoral and 6=nemoral regions



($n=48$), followed by 32 lakes in the coniferous forest ecoregion and 10 lakes in the arctic/alpine ecoregion.

The lakes can be characterized as relatively small (mean lake surface area = 1.1 km^2), nutrient poor (mean TP = $9.8 \text{ } \mu\text{g/L}$ and chlorophyll $a = 3.7 \text{ mg/m}^3$) and situated in forested catchments. Water pH ranged from 4.5 to 7.2 (10 percentile = 5.2 and 90 percentile = 6.9) and buffering capacity (alkalinity/acidity) ranged from -0.062 meq/L to 0.502 meq/L (10th percentile = -0.009 meq/L and 90th percentile = 0.183 meq/L). Inorganic aluminum concentrations averaged $39 \pm 84 \text{ } \mu\text{g/L}$, with concentrations ranging from 0.18 to $668 \text{ } \mu\text{g/L}$ (10th percentile = 2 and 90th percentile = $86 \text{ } \mu\text{g/L}$). The ratio of base cations to the sum of strong acids ranged from 0.54 to 24 (10th percentile = 1.1 and 90th percentile = 6.3).

2.2 Sampling and Analyses

Surface water samples (0–2 m) were collected 4× annually (i.e. spring, summer, autumn and winter) from mid lake using a plexiglas sampler. All chemical determinations were done at the Department of Environmental Assessment and followed international (ISO) or European (EN) standards when available. A number of acidity variables were calculated (see Fölster et al., this volume). All variables with the exception of pH were either $\log_{10}$ or arc-sine of

square-root (proportional data) transformed in order to approximate normally distributed random errors. Hereafter, the physico-chemical variables are referred to collectively simply as water chemistry variables. For a more detailed description of water chemistry variables see Fölster et al. (this issue). Annual mean values were used in the analyses unless otherwise noted.

Littoral macroinvertebrate samples were collected in autumn (September to November) from stony habitats (wind exposed littoral regions) using standardized kick-sampling with a handnet (European Committee for Standardization, 1994), a mesh-size of 0.5 mm, and preserved in 70% ethanol. In the laboratory, samples were processed by sorting under 10× magnification, followed by identification using dissecting and light microscopy. Organisms were identified to the lowest taxonomic unit possible, generally to the species level, although exceptions occurred with some chironomid larvae and immature oligochaetes. Only taxa that occurred in >1% of the lakes were used here, resulting in a species by site matrix of 326 taxa and 126 lakes.

2.3 Statistical Analyses

Both indirect and direct ordinations were used to analyze the importance of water chemical variables on littoral macroinvertebrate community structure. (a) Principal components analysis (PCA) of water chemistry and catchment land use/type and correspondence analysis of macroinvertebrates were used to examine gradients in the data sets. (b) Direct gradient analysis (also known as constrained ordination, ter Braak, 1988, 1990) was used to select environmental variables that could explain significant amounts of the among-lake variability in littoral macroinvertebrate assemblages. Detrended correspondence analysis (DCA) of square-root transformed species abundance, with downweighting of rare taxa, detrending by segments and non-linear rescaling was used to determine the biological turnover, or gradient length, of the species dataset. DCA gave gradient lengths of 3.34 for axis 1 and 2.59 for axis 2, indicating that a unimodal response would adequately fit the species data. Consequently, canonical correspondence analysis (CCA) was used for the constrained ordinations. (c) CCA of macroinvertebrates, geographic position, land use/type, lake hydromorphological descriptors

and water chemistry was used to assess the importance of mean, extreme (minimum and maximum within-year values) and one-year lag-phase responses on littoral communities (i.e. biological variables were compared with physico-chemical variables of the previous year). In CCA species abundance data were square-root transformed and, where necessary, the environmental variables were transformed ($\log_{10}$ or arcsine of square root) in order to approximate normally distributed random errors. Constrained ordinations were run using the species downweighting option and forward selection of environmental variables. Significance of the environmental variables was tested with 999 Monte Carlo permutations. (d) Partial correspondence analysis (pCCA) was used to explore the relationships between the water chemistry and biological response variables (e.g. Borcard, Legendre, & Drapeau, 1992). To analyze for the influence of water chemistry (in particular acid variables) on macroinvertebrate assemblages, geographic position, land use/type, and lake hydromorphological variables were “removed” by running these variables as covariables.

2.4 Establishing Biological Breakpoints

Lakes situated in the mixed forest ecoregion were used to more closely evaluate the relationships between littoral macroinvertebrate assemblages and two selected chemical variables indicative of acid stress (namely, pH and alkalinity/acidity). Scores from the first axis of correspondence analysis of littoral macroinvertebrates (CA axis 1 scores) and Shannon diversity (Shannon, 1948) were regressed against mean annual lake pH and alkalinity/acidity to determine ecological breakpoints or thresholds.

3 Results and Discussion

3.1 Gradient Analysis

Principal components analysis (PCA) of catchment land use and water chemistry for the 90 lakes showed three important environmental gradients (eigenvalues were 17.2, 13.0 and 6.9 for PC axes 1 to 3, respectively) (Table 1). The first PC axis accounted for 31.9% of variance and was strongly related to water chemistry variables indicative of acidity. The

Table 1 PCA loadings (eigenvectors) for the first three axes of principal components analysis of water chemical, land use/type and hydromorphological variables for 90 acid-reference lakes

	PC 1	PC 2	PC 3
Eigenvalue	17.2	13.0	6.9
Percent variance	31.9	24.1	12.7
<i>Geographic variables:</i>			
X coordinate ($\approx$ latitude)	0.117	-0.188	0.139
Y coordinate ($\approx$ longitude)	0.139	-0.017	0.108
<i>Catchment land use, etc.</i>			
catchment area (km ²)	0.124	-0.081	0.088
annual temperature (°C)			
annual precipitation (mm/year)	-0.119	-0.087	-0.073
annual runoff (mm/year)	-0.032	-0.162	0.007
urban (%)	0.030	0.056	-0.017
forest (%)	-0.021	0.148	0.043
open (grassland) (%)	0.006	0.045	-0.056
alpine (%)	0.038	-0.184	-0.034
water (%)	-0.031	-0.025	-0.237
mire (%)	0.051	-0.011	0.245
agriculture (%)	0.003	0.105	-0.144
lake surface area (km ²)	0.115	-0.105	-0.038
lake altitude (m a.s.l.)	-0.025	-0.215	0.103
depth (m)	0.083	-0.106	-0.160
<i>Water physico-chemical variables:</i>			
pH	0.223	0.000	-0.059
alkalinity/acidity (meq/L)	0.227	0.049	-0.016
ANC (meq/L)	0.210	0.110	0.041
ANCalk	0.213	0.101	0.043
ANC/H ⁺	0.229	0.040	-0.037
BC*/SSA*	0.198	-0.005	0.189
BC*/SO ₄ *	0.196	-0.006	0.192
Al _{inorganic} (μg/L)	-0.212	0.024	0.074
Al ³⁺ (μg/L)	-0.220	0.012	0.065
H ⁺ /Al ³⁺	-0.220	0.012	0.065
Ca/Al _{inorganic}	0.219	0.053	-0.100
SO ₄ (meq/L)	-0.060	0.178	-0.240
Cl (meq/L)	-0.091	0.190	-0.188
Al (μg/L)	-0.171	0.083	0.140
TOC (mg/L)	0.004	0.217	0.188
water temperature (°C)	-0.074	0.172	-0.070
conductivity (mS/m)	0.008	0.217	-0.191
NH ₄ -N (μg/L)	-0.160	0.090	0.017
NO ₂ +NO ₃ -N (μg/L)	-0.103	0.121	-0.114
organic-N (μg/L)	0.020	0.242	0.065
PO ₄ -P (μg/L)	-0.058	0.157	0.197
total P (μg/L)	-0.021	0.211	0.138
water color (absorbance 420 nm)	-0.023	0.172	0.274
Secchi depth transparency (m)	0.054	-0.160	-0.269
chlorophyll <i>a</i> (mg/m ³)	-0.041	0.226	0.048

Loadings ≥ 0.20 are marked in bold.

2nd PC axis explained another 24.1% of the variability among lakes and was interpreted as a productivity gradient. For example, chlorophyll *a* and total phosphorus were positively, while altitude and latitude (x coordinates) were negatively associated with the second PC axis. The third PC axis explained 12.7% of the remaining variance and was related to water color (absorbance of filtered water, Secchi depth transparency and catchment land use classified as mire were important descriptors of the third PC axis). Cumulatively, these three gradients: PC1 – acidity, PC2 – latitude/productivity and PC3 – water color explained 68.7% of the variability in land use and water chemistry among the 90 lakes studied here.

Correspondence analysis (CA) of littoral macroinvertebrate assemblages gave eigenvalues of 0.181, 0.157, 0.088 and 0.069, respectively, for the first four axes. Cumulatively, these four axes explained 34.2% of the variance in the species data set; axis 1 to 4 explained 12.5%, 10.9%, 6.1% and 4.7%, respectively, of the variability in community composition. The chironomid midge *Endochironomus* and *Asellus aquaticus* and the stonefly *Capnia atra* and the mayfly *Ameletus inopinatus* were “indicators” for the first CA axis (these taxa were selected as strong preferential or indicator taxa by TWINSPAN, Hill, 1979). *Capnia atra*, restricted for the most part to the arctic/alpine region in the north, indicates nutrient poor conditions, while *Endochironomus* indicates more nutrient-rich lakes in the southern part of the country.

Constrained ordination (CCA) of littoral macroinvertebrate assemblages and geographic position, land use/type, hydromorphological and selected chemical variables (annual mean and within-year extreme values) showed that 13 variables explained 41% of the total variance in littoral macroinvertebrate assemblages. The first three variables selected (alpine catchments, maximum SO₄ concentration and lake surface area) explained 24% of the explained variance. These three variables were interpreted as indicating the importance of a altitude/latitude or productivity gradient, with small, nutrient poor lakes situated in the north and larger, nutrient rich lakes situated in the south. A gradient in lake acidity (pH and buffering capacity) was also evident, with lakes in the south being more affected by SO₄ deposition.

Partial CCA, with non-water chemical variables (e.g. geographic position, land use/type, lake surface

area) as covariables, resulted in nine significant variables that explained 24.2% of the variance in littoral assemblages; 31.8% of the total variance was accounted for by the non-acidic water chemical variables (covariables) and interactions between acidic variables and the non-acidic water chemical variables (Table 2). Three variables indicative of acid stress were amongst the nine significant variables (pH, alkalinity and Al). pH, selected in the first step, accounted for 6% of the variance in macroinvertebrate assemblages among lakes and alkalinity/acidity, selected in the third step, accounted another 3% of the residual variance. Although landscape effects were supposedly removed by running for example geographic position and catchment land use/type as covariables, a number of variables indicative of “lake types” were nonetheless selected in the constrained ordination. For example, minimum water temperature (2%), nutrient variables such as mean PO₄-P (3%) and maximum NO₂+NO₃-N (2%), and mean water color (2%) most likely indicate the influence of a latitudinal gradient on littoral macroinvertebrate assemblages in these lakes.

3.2 Establishing Class Boundaries

Lakes situated in the mixed forest ecoregion were used to evaluate the relationships between lake littoral macroinvertebrate assemblages and water pH and alkalinity/acidity. Both community composition (CA axis 1 scores) and Shannon diversity showed a strong linear relationship with pH. Fitting a quadratic function did not improve the relationship. Linear response curves gave r^2 values of 0.74 and 0.71 for CA axis 1 scores and Shannon diversity, respectively ($p < 0.001$). Root mean square errors of the predictions (RMSE) were 0.53 pH units for CA axis 1 scores and 0.35 pH units for Shannon diversity. Alkalinity/acidity explained between 34% (Shannon diversity) and 40% (CA axis 1 scores) of the variance in the two biological metrics; RMSEs were 0.50 (diversity) and 0.77 (CA axis 1 scores). In contrast to pH, fitting a quadratic function improved the fit between alkalinity/acidity and the two biological variables; r^2 values increase from 40% to 63% for CA axis 1 scores (RMSE=0.61) and from 34% to 57% for diversity (RMSE=0.40).

Table 2 Partial canonical correspondence analysis (pCCA) of littoral macroinvertebrates and environmental variables (mean and extreme values)

Variable	λ_1	model	step
pH	0.06	0.06	1
alkalinity/acidity (meq/L)	0.05	0.03	3
ANC (meq/L)	0.05		
ANCalk	0.05		
ANC/H ⁺	0.05		
BC*/SO ₄ *	0.04		
Al _{inorganic} (μg/L)	0.04		
Al ³⁺ (μg/L)	0.05		
H ⁺ /Al ³⁺	0.05		
Ca/Al _{inorganic}	0.05		
SO ₄ (meq/L)	0.02		
Cl (meq/L)	0.03		
Al (μg/L)	0.04	0.02	7
TOC (μg/L)	0.02		
water temperature (°C)	0.03	0.02	9
conductivity (mS/m)	0.03		
NO ₂ +NO ₃ -N (μg/L)	0.02		
organic-N (μg/L)	0.02		
PO ₄ -P (μg/L)	0.03	0.03	2
total P	0.02		
water color	0.02	0.02	5
(absorbance 420 nm)			
chlorophyll <i>a</i> (mg/m ³)	0.02		
min pH	0.05		
min alkalinity/acidity (meq/L)	0.04		
min ANC (meq/L)	0.05		
min ANCalk (meq/L)	0.05		
minANC/H ⁺	0.05		
min BC*/SSA*	0.05		
min BC*/SO ₄ *	0.05		
max Al _{inorganic} (μg/L)	0.04		
max Al ³⁺ (μg/L)	0.05		
max H ⁺ /Al ³⁺	0.05		
min Ca/Al _{inorganic}	0.05		
max SO ₄ (meq/L)	0.02		
max Cl (meq/L)	0.03		
max TOC (μg/L)	0.02		
min water temperature (°C)	0.02	0.02	6
min conductivity (mS/m)	0.03	0.03	4
max NO ₂ +NO ₃ -N (μg/L)	0.02	0.02	8
min Org-N (μg/L)	0.03		
min PO ₄ -P (μg/L)	0.02		
min total P (μg/L)	0.02		
max water color	0.02		
(absorbance 420 nm)			
min chlorophyll <i>a</i> (mg/m ³)	0.01		
<i>total inertia (variance)</i>		<i>1.446</i>	
<i>Sum of all unconstrained eigenvalues (after fitting covariables)</i>		<i>0.986</i>	

Table 2 (continued)

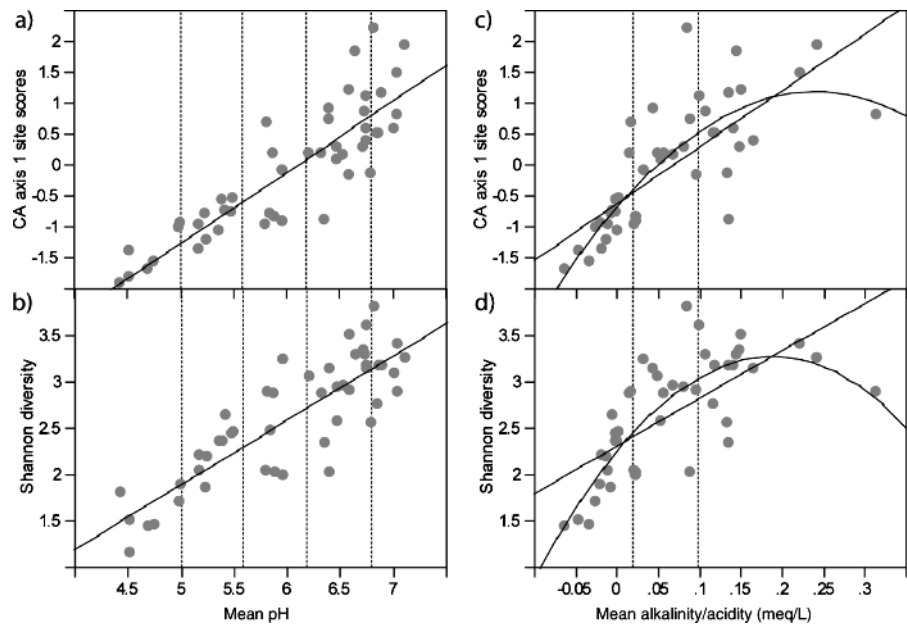
Variable	λ_1	model	step
<i>Sum of all canonical eigenvalues (after fitting covariables)</i>		<i>0.239</i>	

The influence of water chemical variables was analyzed by removing the effect of landscape and other descriptors by running these variables as covariables. All variables selected explained significant amounts of among-lake variability ($p < 0.001$). “Lamda 1” (λ_1) shows the unconstrained variance of the individual explanatory variables (i.e. the marginal effect of the single variables), “model” shows the additional variance each variable explains at the time it was included in the model (i.e. the conditional effect), and “step” shows the order of inclusion in the model. For more information of the water chemistry variables see Fölster et al. (this issue).

Both CA axis 1 scores and Shannon diversity showed a funnel-shaped response when regressed against the two acidity variables (Fig. 2). Low variance, which can be interpreted as an indication of stress, was evident at pH values < 5 and alkalinity/acidity values < 0.02 meq/L. The finding that benthic macroinvertebrates in Swedish lakes are responding to acidity is not novel, but supports earlier studies of biological response to acidification. For example, J. Økland and K. A. Økland (1986) argued that gastropods were sensitive to changes in pH, and these authors noted a loss of species richness between pH 6.2 and 5.9, and no gastropods were recorded at $\text{pH} \leq 5.2$. Fish have also been used as an indicator for assessing the effects of acidification on aquatic ecosystems. Critical load work with fish has used an alkalinity value of 0.05 meq/L as a threshold below which biological effects are predicted to occur (e.g. Lien, Raddum, Fjellheim, & Henriksen, 1996).

Five classes were used to summarize the effects of water pH on littoral macroinvertebrate assemblages. These classes were established by visual examination of the regression plot and using literature data (e.g. Lükewille et al., 1997). The selected cutoffs for the five classes were $\text{pH} < 5$ (extremely acid), $5 < \text{pH} \leq 5.6$ (very acid), $5.6 < \text{pH} \leq 6.2$ (acid), $6.2 < \text{pH} \leq 6.8$ (weakly acid) and $\text{pH} > 6.8$ (neutral-alkaline). The extremely acid and very acid classes showed low variance around the regression line for both biological variables. Moreover, these two cut levels agree with findings of number of studies showing ecological impairment at $\text{pH} < 6$ (e.g. Raddum & Fjellheim,

Fig. 2 Regression plots of CA axis 1 scores and Shannon diversity against mean pH and mean alkalinity/ acidity for lakes situated in the mixed forest ecoregion. Curved lines show quadratic fit. Horizontal dashed lines show ecological boundaries (see text)



1984; Lingdell & Engblom, 2002). The acid class ($5.6 < \text{pH} \leq 6.2$) was indicated by an increase in residual variance around the regression line. Although the number of sites in this pH interval was low ($n=7$ lakes), approximately half of the lakes had relatively high and the other half had low ecological status. The final two classes (weakly acid and neutral-alkaline) are defined at $\text{pH} > 6.2$. The five classes suggested here agree to some extent with cut levels for pH currently used in Norway (i.e. $\text{pH}=5.0, 5.5, 6.0$ and 6.5 ; Lükewille et al., 1997).

In contrast to pH, only three classes were established for alkalinity/acidity. Similar to the findings for pH, the residual variance around the regression line seemed to collapse at low alkalinity/acidity values < 0.02 meq/L. At alkalinity/acidity between 0.02 and 0.1 meq/L residual variance was considered moderate, and at values > 0.1 meq/L residual variance was high. The finding that alkalinity/acidity < 0.020 meq/L is critical for macroinvertebrates lends support to the study by Lien et al. (1996); these authors suggested 0.020 meq/L as the tolerance-level for fish and macroinvertebrate assemblages of Norwegian surface waters. Raddum and Skjelkvåle (1995) in a review of European lakes and rivers argue, however, that this critical threshold is relevant only for systems with low Ca concentrations. For lakes and streams with high

Ca concentrations (i.e. high ionic strength) the authors recommended a threshold of 0.050 meq/L.

Organism response to acidification is complex, reflecting both the direct physiological effect of pH as well as the effects of associated toxic metals and indirect effects mediated through bottom-up processes (e.g. food availability), and a number of studies have shown that macroinvertebrates, in particular mayflies, are affected directly by low pH and high concentrations of inorganic aluminium (e.g. Ormerod et al., 1987). Rosseland, Eldhuset, and Staurnes (1990) found that aquatic organisms were affected by inorganic Al concentrations $> 25 \mu\text{g/L}$ and these authors suggested this value as a lower threshold below which biological effects are negligible and a second concentration of $75 \mu\text{g/L}$ was suggested as an upper threshold where strong effects were predicted. Our findings showed that littoral communities in many lakes in southern Sweden are still indicating signs of acid stress. Although Al fractions were used in our analyses, we found pH and alkalinity/acidity to be better predictors of the among-lake variability in assemblage composition. However, since this work is entirely based on correlation we cannot draw causal inference, and pH and alkalinity may be regarded as proxies for many covarying variables such as inorganic Al. Clear biological thresholds were difficult to ascertain, hence residual variance

of regression plots and literature values were used to establish five ecological classes for pH and three classes for alkalinity/acidity.

Acknowledgements Thanks to the many people involved in the sampling and processing of the water chemistry and macroinvertebrate samples. In particular, we thank Björn Wiklund for sorting and Lars Eriksson for identifying the macroinvertebrates. Financial support for this project was provided by the Swedish Environmental Protection Agency and the EU-funded Integrated Project Euro-Limpacs (6th Framework Programme; contract number: GOCE-CT-2003-505540).

References

- Bernes, C. (1991). Acidification and liming of Swedish freshwaters. Swedish Environmental Protection Agency. *Monitor*, 12, 144.
- Borcard, D., Legendre, P., & Drapeau, P. (1992). Partialling out the spatial component of ecological variation. *Ecology*, 73, 1045–1055.
- European Committee for Standardization (1994). Water quality-methods for biological sampling – guidance on handnet sampling of aquatic benthic macro-invertebrates. *SS-EN-27-828. European Committee for Standardization*. Brussels, Belgium.
- Fölster, J., Andren, C., Bishop, K., Buffam, I., Cory, N., Goedkoop, W., et al. (this issue). New environmental quality criteria for acidification in lakes in Sweden – an application of studies on the relationship between biota and waterchemistry. *Water, Air and Soil Pollution*.
- Halvorsen, G. A., Heegaard, E., Fjellheim, A., & Raddum, G. G. (2003). Tracing recovery from acidification in the western Norwegian Nausta Watershed. *Ambio*, 32, 235–239.
- Hill, M. O. (1979). *TWINSPAN – A FORTRAN program for arranging multivariate data in an ordered two-way table by classification of the individuals and attributes*. Ithaca: Cornell University.
- Lien, L., Raddum, G. G., Fjellheim, A., & Henriksen, A. (1996). A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. *The Science of the Total Environment*, 177, 173–193.
- Lingdell, P.-E., & Engblom, E. (2002). Bottendjur som indikator på kalkningseffekter. Swedish EPA report 5235. Naturvårdsverkets förlag.
- Lükewille, A., Jeffries, D., Johannessen, M., Raddum, G., Stoddard, J., & Traaen, T. S. (1997). The nine year report: acidification of surface water in Europe and North America. Long-term Developements (1980s and 1990s), *Norsk institut for vannforskning (NIVA)*, 1997; 168pp.
- Økland, J., & Økland, K. A. (1986). The effects of acid deposition in benthic animals in lakes and streams. *Experientia*, 42, 471–486.
- Ormerod, S. J., Boole, P., McCahon, C. P., Weatherley, N. S., Pascoe, D., & Edwards, R. W. (1987). Short-term experimental acidification of a Welsh stream: comparing the biological effects of hydrogen ions and aluminium. *Freshwater Biology*, 17, 341–356.
- Raddum, G. G., & Fjellheim, A. (1984). Acidification and early warning organisms in freshwater in western Norway. *Verhandlungen der Internationalen Vereinigung der Theoretischen und Angewandte Limnologi*, 22, 1973–1980.
- Raddum, G. G., & Skjelkvåle, B. L. (1995). Critical limits of acidification to invertebrates in different regions of Europe. In *Aquatic fauna: Dose/response and long term trends. CLRTAP-International cooperative programme on assessment and monitoring of acidification of rivers and lakes* (pp. 26–34). Norway: University of Bergen.
- Rosseland, B. O., Eldhuset, T. D., & Staurnes, M. (1990). Environmental effects to aluminium. *Environmental Geochemistry and Health*, 12, 17–27.
- Shannon, D. E. (1948). A mathematical theory of communication. *Bell System Technological Journal*, 27, 379–423, 623–656.
- Stendera, S., & Johnson, R. K. Recovery trends of phytoplankton and benthic macroinvertebrate communities in acidified and reference boreal lakes – a multihabitat assessment (submitted).
- Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., et al. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature*, 401, 575–578.
- ter Braak, C. F. J. (1988). CANOCO – a FORTRAN program for canonical community ordination by [partial] [detrended] [canonical] correspondence analysis, principal component analysis and redundancy analysis (version 3.15). Agricultural Mathematics Group, Wageningen, The Netherlands.
- ter Braak, C. F. J. (1990). Update notes: CANOCO version 3.10. Agricultural Mathematics Group, Wageningen, The Netherlands.
- Wilander, A. (1997). Referenssjöarnas vattenkemi under 12 år; tillstånd och trender. *Naturvårdsverket Rapport*, 4652, 79 (in Swedish).

A Novel Environmental Quality Criterion for Acidification in Swedish Lakes – An Application of Studies on the Relationship Between Biota and Water Chemistry

Jens Fölster · Cecilia Andrén · Kevin Bishop ·
Ishi Buffam · Neil Cory · Willem Goedkoop ·
Kerstin Holmgren · Richard Johnson ·
Hjalmar Laudon · Anders Wilander

Received: 12 June 2005 / Accepted: 3 April 2006 / Published online: 27 January 2007
© Springer Science + Business Media B.V. 2007

Abstract The recovery from acidification has led to the demand for more precise criteria for classification of acidification. The Swedish Environmental Protection Agency has revised Sweden's Ecological Quality Criteria for acidification to improve the correlation between the chemical acidification criteria and bio-

logical effects. This paper summarises the most relevant findings from several of the studies commissioned for this revision. The studies included data on water chemistry in 74 reference lakes in southern Sweden with data on fish in 61 of the lakes, as well as data on littoral fauna in 48 lakes. We found that the acidity variable most strongly correlated to the biota was the median pH from the current year. Our results probably do not reflect the mechanisms behind the negative effects of acidity on the biota, but are fully relevant for evaluation of monitoring data. The biogeochemical models used for predicting acidification reference conditions generate a pre-industrial buffering capacity. In order to get an ecologically more relevant criteria for acidification based on pH, we transferred the estimated change in buffering capacity into a corresponding change in pH. A change of 0.4 units was defined as the threshold for acidification. With this criterion a considerably lower number of Swedish lakes were classified as acidified when compared with the present Ecological Quality Criteria.

J. Fölster (✉) · K. Bishop · W. Goedkoop · R. Johnson ·
A. Wilander
Department of Environmental Assessment, SLU,
Box 7050, 750 07 Uppsala, Sweden
e-mail: Jens.Folster@ma.slu.se

C. Andrén
Department of Applied Environmental Science,
Stockholm University, ITM,
106 91 Stockholm, Sweden

I. Buffam
Department of Forest Ecology, SLU,
901 83 Umeå, Sweden

N. Cory
Forest Resource Management and Geomatics, SLU,
Skogsmarksgränd,
901 83 Umeå, Sweden

K. Holmgren
National Board of Fisheries,
178 93 Drottningholm, Sweden

H. Laudon
Department of Ecology and Environmental Sciences,
Umeå University,
901 87 Umeå, Sweden

Keywords fish · monitoring · littoral fauna ·
water chemistry

1 Introduction

In Sweden, a set of official Environmental Quality Criteria for surface waters (EQC) have been used for

evaluation of monitoring data since 1990. In the EQC, anthropogenic impact is assessed using the ratio between an observed value and a modelled value of pre-industrial reference conditions (Swedish Environmental Protection Agency, 2000). This ratio is referred to as an Ecological Quality Ratio, EQR. As acid deposition declines, the demand for accuracy in the criteria for classification of acidification has increased. This is because as surface waters recover and approach pre-industrial reference condition chemistry, we need to know whether acidification is still an environmental problem of a magnitude that motivates further expensive actions to reduce emissions. When acidification was higher, it was not as important to know exactly what degree of acidification existed.

Another reason for the EQC revision is that implementation of the EU Water Framework Directive calls for more ecological relevance in the application of chemical EQC for water chemistry. In Sweden, where 20 million Euros are spent annually to mitigate acidification by liming, it is also important to assess when liming can be reduced, without risk of ecological damage from reacidification. In response to these demands, the Swedish Environmental Protection Agency (SEPA) initiated a number of research projects to give a basis for new EQC for acidification with a better correlation of the chemical acidification criteria to biological effects than the present EQC.

In the current EQC for acidification, anthropogenic impact is measured as a decrease in alkalinity (Alk), and the EQR is calculated as Alk/Alk_0 , where Alk_0 is a reference value modelled with an F-factor model proposed by Bernes (1991). When the EQR is <0.75 , the water is classified as acidified. The EQC for acidification has been disputed for two reasons. Firstly, the correlation of the ratio Alk/Alk_0 to biological effects is poor. In very alkaline waters, the biological effects of an EQR of 0.75 is negligible. For weakly buffered waters, on the other hand, biological effects may occur at smaller changes in the alkalinity. Secondly, the F-factor model has been shown to give systematic errors during recovery from acidification (Rapp, 1998). The present paper reports the work on finding an ecologically relevant criterion for acidification impact. The work with improved prediction of reference values will be reported elsewhere.

An alternative to an EQR threshold for anthropogenic impact is to use critical values of an acidity parameter. In calculations of Critical Loads for acid

deposition, for example, a critical value of Acid Neutralising Capacity (ANC), $\text{ANC}_{\text{limit}}$, of 20 $\mu\text{eq/l}$ is used (Henriksen, Kämäri, Posch, & Wilander, 1992; Lien, Raddum, Fjellheim, & Henriksen, 1996). The $\text{ANC}_{\text{limit}}$ was based on studies of relationships between biology and water chemistry in Norwegian lakes and streams. However, these waters are less humic than many of those in Sweden. The maximum concentration of Total Organic Carbon (TOC) in Lien's et al. (1996) study of Norwegian waters was less than 4 mg/l, while the median concentration of TOC in Swedish lakes was 9.8 mg/l (Wilander, Johnson, & Goedkoop, 2003). It has thus been questioned whether an $\text{ANC}_{\text{limit}}$ of 20 $\mu\text{eq/l}$ is relevant as a threshold for biological damage in Swedish waters. In an initial study on the relationship between presence of roach and acidity in Swedish lakes, an $\text{ANC}_{\text{limit}}$ several times higher was suggested (Andersson, Appelberg, & Wilander, 2001). In this study the presence of roach was more closely correlated to pH than to either ANC or Alk. The appropriateness of ANC was also questioned by Lydersen, Larssen, and Fjeld (2004) who suggested a modified ANC where a fraction of the organic anions were regarded as strong acids.

It is well established that fish toxicity in acidic systems can be related to both low pH and elevated inorganic aluminium, Ali (e.g. Cronan & Schofield, 1979). Mechanisms for aluminium toxicity have been proposed (Exley, Chappell, & Birchall, 1991). Other indicators such as ANC/H^+ and Ca/Ali have also been found to give a good correlation to fish mortality (Laudon, Poleo, Vollestad, & Bishop, 2005).

This paper summarises the most relevant findings from the studies initiated by SEPA where different acidity indicators were evaluated with respect to the relevance for littoral fauna and fish in lakes (Cory & Andrén, 2004; Holmgren & Buffam, 2005; Johnson, Goedkoop, & Wilander, 2004). Based on these results, we suggest a new criterion of acidification impact for the EQC related to changes in pH.

2 Materials and Methods

The study included 74 lakes which are part of national and regional monitoring programs. They are relatively small, with forest dominated catchments and they are not influenced by point source pollution. The study

lakes are representative of the range of lakes in Sweden with the exception that eutrophic and dystrophic lakes are underrepresented (Johnson, 1999). In our study we restricted the data to lakes in southern Sweden (Fig. 1). The reason for this was that the statistical analysis was compromised by a number of lakes in northern Sweden that lacked fish due to reasons other than acidity. This restriction is also relevant for our study since lake acidification is predominantly a problem in southern Sweden.

Littoral fauna samples were collected in 48 of the 74 study lakes. The samples were taken in autumn from stony habitats using standardized kick-sampling with a handnet of mesh size 0.5 mm. Organisms were identified to the lowest taxonomic unit possible, generally to the species level. The littoral fauna was represented both as the first axis of a Correspondence analysis (CA) and by an acidity index (Swedish Environmental Protection Agency, 2000).

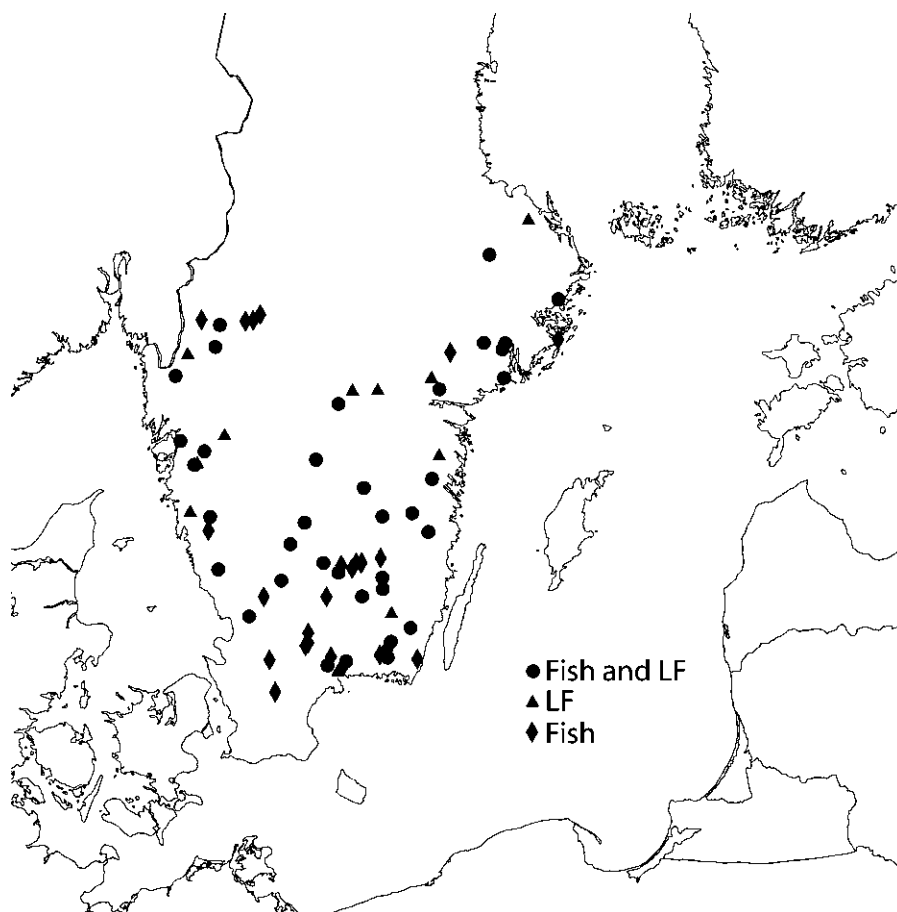
Fish were sampled in 64 of the study lakes with multi-mesh gillnets following standard protocols.

Fish were represented as presence/absence of acid sensitive species or size classes (Holmgren & Buffam, 2005). In southern Sweden, presence of small roach (<100 mm) is most often a good indicator of acidification.

Lake water chemistry was sampled at least four times a year. All water chemistry determinations were made according to ISO standards. The method used for alkalinity (Alk) in the Swedish monitoring programs, (ISO 9963-2) includes a titration down to pH 5.6 while the sample is purged with N₂ to remove CO₂. The method gives an alkalinity close to the carbonate alkalinity since only a small amount of organic acids are titrated at such a high titration end point. In samples where pH was less than 5.6, the acidity was measured by titration with a base up to the same pH.

An alternative estimate of buffering capacity is ANC which is calculated as the difference between base cations (BC) and strong acid anions (SAA). A modified ANC (ANC_{mod}) was also calculated to

Fig. 1 Southern Sweden showing locations of the 74 lakes included in this study



account for the fact that up to ca 2/3 of the organic anions are strong acid anions, i.e. not buffering within the pH range of natural waters. This ANC_{mod} was defined as Eq. 1:

$$ANC_{mod} = \text{Alkalinity}(\text{meq/l}) + \beta\text{TOC}(\text{mg/l}) \quad (1)$$

with β -values between 0 and 6.3, where 6.3 is the charge density at pH 5.6 (Köhler, Laudon, Wilander, & Bishop, 2000). The different modified ANC-values correspond to fractions between 0 and c. 2/3 of the organic anions being strong acid anions.

Inorganic Aluminium, Al_i , is routinely determined within Swedish acidification and liming monitoring using the cation exchange method (Driscoll, 1984), as described in Andrén (1995). In the data used in this study, laboratory fractionation is not comprehensive. Instead we used Al_i modelled with the chemical equilibrium model WHAM (Tipping, Berggren, Mulder, & Woof, 1995), after calibration of the model to Swedish waters (Cory & Andrén, 2004).

Besides these common acidity indicators, a range of alternative chemical acidity indicators were also tested: ANC/H^+ , BC/SAA , Al^{3+} , $H^+ + Al^{3+}$ and Ca^{2+}/Al_i .

Calculation of pH from ANC and TOC was done using the charge balance Eq. 2:

$$ANC = (OH^- + HCO_3^- + 2CO_3^{2-} + RCOO^- - H^+ - nAl^{n+}) \quad (2)$$

HCO_3^- and CO_3^{2-} were calculated with the equilibrium equations for the carbonate system by setting the pCO_2 to four times the background partial pressure in the atmosphere. Organic acids, $RCOO^-$, were calculated using the triprotic model proposed by Köhler et al. (2000).

3 Results and Discussion

3.1 Selecting Acidity Indicator

For both littoral fauna and fish, pH was generally the most strongly correlated acidity variable. The correlation of Alk, and Al_i with the biota was either similar or weaker than for pH (Figs. 2 and 3). ANC was more poorly correlated to biota than Alk. The performance of ANC_{mod} was intermediate between

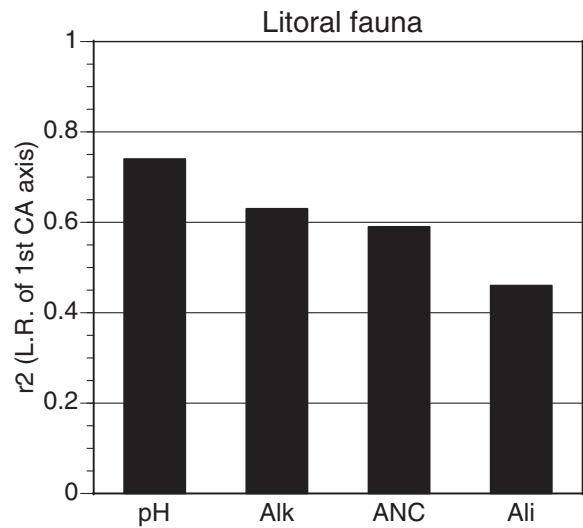


Fig. 2 The r^2 for linear regression of the first CA axis of littoral fauna against medians for pH, Alk, ANC and Al_i in lakes in southern Sweden

those of ANC and Alk (data not shown). Similar results were found for the less common acidity indicators. The results are in accordance with the study on roach by Andersson et al. (2001), although that study did not include Al_i . The toxicity of Al_i is well established. Therefore a better correlation with Al_i could have been expected, however, it is noted that most studies have concerned the effects of Al_i on salmonids in streams.

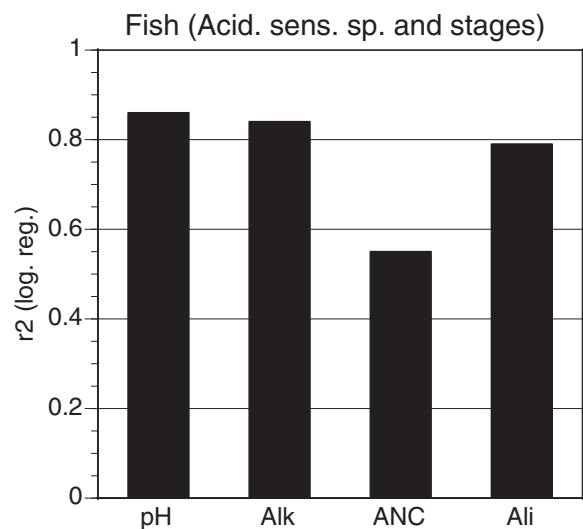


Fig. 3 Nagelkerke r^2 for logistic regression of presence/absence of acid sensitive stages of fish in relation to median pH, Alk, ANC and Al_i of lakes in southern Sweden

The relatively poor correlation of biota to Al_i in our studies could be due to the lack of sampling at critical periods such as spring snow melt. Additional errors could also be introduced by using modelled data on Al_i , instead of measured concentrations, as well as the analytical error of the Al_i values used to calibrate the model.

Lake water chemistry varies over time with more acid conditions after periods of high precipitation and more well buffered chemistry during dry periods. The magnitude of the variation and the response time to the change in hydrology depends on catchment area and lake turnover times. Several studies in streams have shown that the biota is controlled by the extreme acidic situations during high flow periods (Baker et al., 1996; Laudon et al., 2005). We expected to find a similar relationship in lakes, although with lower variability. This was, however, not the case in our data. The regressions between pH and biota did not improve significantly when the minimum pH was used instead of the median pH. A complicating factor is that the extreme situations during, for example, spring snow melt, are seldom represented by water samples taken only four times a year. The annual minimum values will then have a large variation and include both extreme and more stable conditions. To test this, water chemistry during years with unusually acid conditions were compared with observations of biota. Still, the extreme value was not better correlated to biota than the median value. One reason for this might be that the extreme situation does not always correspond to the season when biota are most sensitive to acidity (McCormick & Leino, 1999). For littoral fauna, there is also a possibility of recolonisation between the extreme situation and the autumn sampling. From our results, we cannot conclude whether the extreme or the average situation controls biota. Since the median chemistry and extreme chemistry are well correlated in many regards, it is expected that the median chemistry correlates to the biota even if the critical values would occur at peak flow. Due to the difficulty in consistently observing critical but transient situations during routine monitoring, the use of median values would seem preferable in the evaluation of monitoring data.

The current annual median gave generally as good or better correlations to both littoral fauna and fish as the 1-year lag or 3 year median. Our results contrast

partly with what we envisaged for the relationship between water chemistry and biota. We expected that extreme values should be better correlated to biota than the median or mean values, and that there would be a “memory” effect from earlier acid conditions captured by time-lags or long-term means of the data. For fish at least we considered Al to be a more important predictor than demonstrated in our results. For fish we also expected a better correlation of water chemistry with a lag time of 1 year than for the current year since the most sensitive stages occur at least 1 year before the fish are caught in the gill nets. Instead it was the median pH of the current year that was the best acidity variable for both fish and littoral fauna. The large variety of lake size, turnover time, and humic content in the data set may help explain this. Furthermore, the sampling frequency for many lakes was too low to cover the inter-annual variation. It is possible that with a more homogeneous dataset or with a higher sampling frequency, the findings would better reflect expected correlations. However, the data provide good coverage of the range of lakes and sampling frequency that EQC are meant to be applied to. Thus the results are fully relevant for our purpose.

3.2 How Shall Acidification be Assessed?

Our studies suggested that pH is the preferred acidity index. The use of measured pH is however problematic, since it is sensitive to changes in TOC and CO_2 pressure, pCO_2 . pH can also change during sample handling due to degassing of CO_2 , and the risk for analytical error is large in waters with low ionic strength. In this study, the high correlation of pH to biota was found for median values of at least four samples from 1 year where sample handling and determination were well standardised. This cannot be taken for granted in all monitoring programs. Also due to the labile nature of pH, most biogeochemical models calculate reference conditions in terms of buffering capacity.

Our solution to this problem is to translate the change in buffering capacity between the present and the predicted pre-industrial reference value, into a change in pH (ΔpH). In other words, present and pre-industrial pH values are calculated from the present and pre-industrial ANC values. This is done using chemical equilibrium equations and includes the

assumption that TOC has remained constant since pre-industrial conditions. The $p\text{CO}_2$ is also assumed to be constant over time and was set to four times the background value in air, which was the average $p\text{CO}_2$ in the lakes included in the study. In reality both TOC and $p\text{CO}_2$ are likely to have changed due to climate variability and changes in land use (Clair et al., 2002; Pastor et al., 2003). By fixing the TOC and $p\text{CO}_2$ we do not estimate the actual change in pH, but rather how much deposition of strong acids has depressed pH under the current climate and land use. In a recent paper, it was suggested that acidification might depress TOC concentrations (Evans, Monteith, & Cooper, 2005) which would give us an overestimation of the pH change caused by acid deposition. Until this effect has been quantified, however, we assume it to be negligible.

One source of error in the calculation of ΔpH is that Al was not included in the chemical equilibrium model. At low pH, when the concentration of cationic Al and its pH buffering can be substantial, the model will underestimate the pH. This is not seen as a problem for the application of the EQR, since it will give an overestimation of the ΔpH when cationic Al is present. The calculated ΔpH will then be an approximation of the increase in total acidity.

In the proposal for new EQC, a change in pH of 0.4 units was set as the limit for acidification. This corresponds approximately to a change of one unit in the biological acidification index used in the EQC for

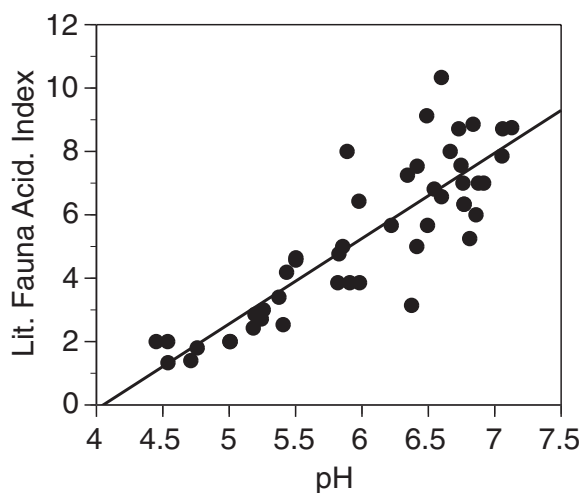


Fig. 4 Medin's acidity index against mean pH for lakes in southern Sweden

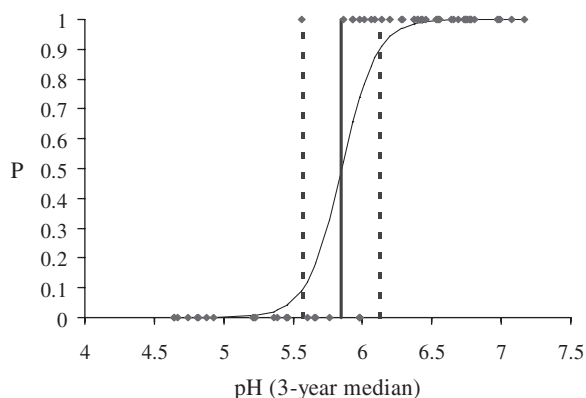


Fig. 5 Logistic regression of presence of acid sensitive species and stages of fish against pH of lakes in southern Sweden

littoral fauna (Fig. 4). The 0.4 unit pH decline is also slightly more than the difference between the 10 and 90% levels in the logistic regression of acid sensitive fish in southern Sweden (Fig. 5). Due to the logarithmic scale of pH, an absolute change is more appropriate than a pH ratio. A ΔpH of 0.4 is equal to a hydrogen ion ratio ($\text{H}_0^+/\text{H}_t^+$) of 0.398.

When we compare ΔpH as the criterion for acidification with the presently used ratio Alk/Alk_0 , we find that the former gives a lower number of acidified lakes in Sweden. In the national lake survey 2000 (Wilander et al., 2003), only 2.6% of 3,464 lakes were acidified, according to the criteria $\Delta\text{pH} > 0.4$. With the criteria of $\text{Alk}/\text{Alk}_0 < 0.75$, 8.9% were considered

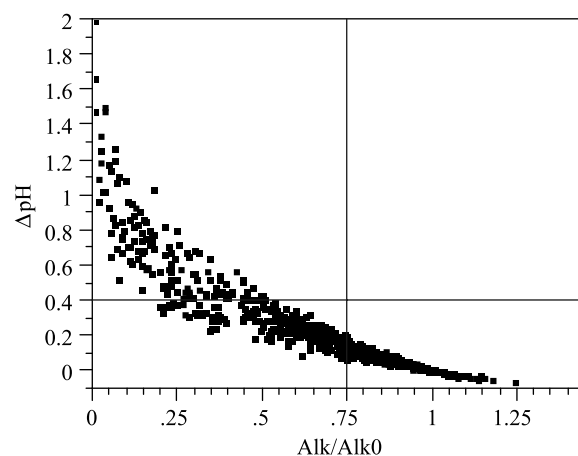


Fig. 6 Comparison of two criteria for acidification for the national lake survey 2000 in Sweden. For ΔpH , the limit for acidification was set to 0.4, and for Alk/Alk_0 , the limit was 0.75

acidified. In both cases the reference value was calculated with the F-factor model used in the Swedish EQC. A comparison of the two criteria shows that there are a large number of lakes in the lake survey that were classified as acidified with the present EQC, where the corresponding change in pH was too small to have had a significant effect on the biota (Fig. 6).

4 Conclusions

We found that median pH from the current year was the acidity variable most consistently and strongly correlated to the biota. Our results probably do not reflect the mechanisms behind the negative effects of acidity on the biota, where Al_i and extreme situations are likely to be more important. However, our results are fully relevant for evaluation of monitoring data where extreme situations are not likely to be sampled.

The biogeochemical models used for predicting acidification reference conditions generate a pre-industrial ANC. In order to obtain an ecologically relevant criteria for acidification, we transferred the estimated change in ANC into a corresponding change in pH, where a change of 0.4 units was defined as the limit for acidification. With this criterion a considerably lower number of Swedish lakes were classified as acidified compared to the present EQC.

Compared to the present Swedish EQC, the suggested new chemical criterion for acidification is better correlated to biological effects. Therefore it will be more reliable for setting targets for reductions in emissions and adapting the liming policy to the decreasing levels of acid deposition.

Acknowledgements This report is based on data from monitoring programs funded by the Swedish Environmental Protection Agency.

References

- Andersson, H. C., Appelberg, M., & Wilander, A. (2001). Gränsvärden för förurning ur svenska fiskars perspektiv. (Engl. summary: Critical chemical values based on Swedish condition). In: Sötvatten. Årsskrift för miljöövervakningen 2001. ISBN 91-620-5149-0, 24–27.
- Andrén, C. (1995). Aluminium speciation; effects of sample storage. *Water, Air and Soil Pollution*, 85, 811–816.
- Baker, J. P., VanSickle, J., Gagen, C. J., DeWalle, D. R., Sharpe, W. E., Carline, R. F., et al. (1996). Episodic acidification of small streams in the northeastern United States: Effects on fish populations. *Ecological Applications*, 6, 422–437.
- Bernes, C. (1991). Acidification and liming of Swedish freshwaters. ISBN 91-620-1109-X. Swedish Environmental Protection Agency, Solna.
- Clair, T. A., Ehrman, J. M., Ouellet, A. J., Brun, G., Lockerbie, D., & Ro, C. U. (2002). Changes in freshwater acidification trends in Canada's Atlantic Provinces: 1983–1997. *Water, Air and Soil Pollution*, 135, 335–354.
- Cory, N., & Andrén, C. (2004). *Modelling of aluminium speciation as a complement to laboratory-based analysis*. Uppsala, Dep. of Environ. Assess., Swedish University of Agricultural Sciences. Report 2004:12. ISSN 1403–977X.
- Cronan, C. S., & Schofield, C. L. (1979). Aluminium leaching response to acid precipitation: Effects on high-elevation watersheds in the northeast. *Science*, 204, 304–306.
- Driscoll, C. T. (1984). A procedure for the fractionation of aqueous aluminium in dilute acidic water. *International Journal of Environmental Analytical Chemistry*, 16, 267–284.
- Evans, C. D., Monteith, D. T., & Cooper, D. M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, 137(1), 55–71.
- Exley, C., Chappell, J. S., & Birchall, J. D. (1991). A mechanism for acute aluminum toxicity in fish. *Journal of Theoretical Biology*, 151, 417–428.
- Henriksen, A., Kämäri, J., Posch, M., & Wilander, A. (1992). Critical loads of acidity: Nordic surface water. *Ambio*, 21, 356–363.
- Holmgren, K., & Buffam, I. (2005). Critical values of different acidity indices – as shown by fish communities in Swedish lakes. *Verhandlungen der Internationalen Vereinigung für Theoretische und Angewandte Limnologie*, 29, 654–660.
- Johnson, R. K. (1999). Regional representativeness of Swedish reference lakes. *Environment and Man*, 23, 115–124.
- Johnson, R. K., Goedkoop, W., & Wilander, A. (2004). *Relationships between macroinvertebrate communities of stony littoral habitats and water chemistry variables indicative of acid-stress*. Report 2004:6, pp. 35. Dep. of Environ. Assess., Swedish Univ. of Agr. Sci.
- Köhler, S., Laudon, H., Wilander, A., & Bishop, K. (2000). Estimating organic acid dissociation in natural surface waters using total alkalinity and TOC. *Water Research*, 34, 1425–1434.
- Laudon, H., Poleo, A. B. S., Vollestad, L. A., & Bishop, K. (2005). Survival of brown trout during spring flood in DOC-rich streams in northern Sweden: the effect of present acid deposition and modelled pre-industrial water quality. *Environmental Pollution*, 135, 121–130.
- Lien, L., Raddum, G. G., Fjellheim, A., & Henriksen, A. (1996). A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. *Science of the Total Environment*, 177, 173.

- Lydersen, E., Larssen, T., & Fjeld, E. (2004). The influence of total organic carbon (TOC) on the relationship between acid neutralizing capacity (ANC) and fish status in Norwegian lakes. *Science of the Total Environment*, 326 (1–3), 63–69.
- McCormick, J. H., & Leino, R. L. (1999). Factors contributing to first-year recruitment failure of fishes in acidified waters with some implications for environmental research. *Transactions of the American Fisheries Society*, 128, 265–277.
- Pastor, J., Solin, J., Bridgham, S. D., Updegraff, K., Harth, C., Weishampel, P., et al. (2003). Global warming and the export of dissolved organic carbon from boreal peatlands. *Oikos*, 100, 380–386.
- Rapp, L. (1998). Critical loads for surface waters: Validation and challenges. Licentiate Thesis, pp. 23, Swedish University of Agricultural Sciences, Umeå.
- Swedish Environmental Protection Agency (2000). *Environmental quality criteria – lakes and watercourses*. Report 5050. ISBN 91-620-5050-8. Kalmar.
- Tipping, E., Berggren, D., Mulder, J., & Woof, C. (1995). Modeling the solid-solution distributions of protons, aluminum, base cations and humic substances in acid soils. *European Journal of Soil Science*, 46, 77–79.
- Wilander, A., Johnson, R. K., & Goedkoop, W. (2003). Riksinventering 2000, Institutionen för Miljöanalys, SLU. Rapport 2003:1. ISSN 1403-977X.

Effects of Liming on the Aquatic Fauna in a Norwegian Watershed: Why Do Crustaceans and Fish Respond Differently?

Trygve Hesthagen · Bjørn Walseng ·
Leif Roger Karlsen · Roy M. Langåker

Received: 16 June 2005 / Accepted: 15 October 2006 / Published online: 17 January 2007
© Springer Science + Business Media B.V. 2007

Abstract We studied the effects of liming on fish and crustaceans in a watershed which is in a region known to have one of the highest diversity of aquatic biota in Norway. This watershed, Enningdal, is shared between Norway (1/3) and Sweden (2/3) and includes 61 lakes > 1.0 ha in Norway. Liming started on a large scale in the 1980s. Currently, a total of 26 of lakes (43%) are limed, covering 93% of the total lake area. The mean value±S.D. of pH and the concentration of inorganic labile Al in these lakes is 6.62 ± 0.35 and $3 \pm 4 \mu\text{g l}^{-1}$, respectively. Historical data of fish communities have been obtained from surveys, while test-fishing and sampling of crustaceans were conducted in 24 lakes in recent years (2002–2004). The present study shows that crustaceans to a greater extent than fish has responded to improved water quality after more than 20 years of liming. Of a total

of 120 fish populations, 42 (35%) have gone extinct. Only five of the lost fish populations (12%) have been re-established, all due to human re-introductions. Physical barriers are considered to be the main factor preventing fish from invading limed lakes. In contrast, crustaceans have been re-established in most limed lakes. This may be mainly due to their good spreading capacity. However, they might also have survived in refuges within the watershed, or as resting-eggs in the sediment.

Keywords acidification · liming · recovery rate · crustaceans · fish

1 Introduction

Reduced crustacean and fish diversity caused by acidification is well documented (Schindler et al., 1991). Responses vary, however, both from species to species and between developmental stages. In Norway, acidification has wiped out nearly 10 000 fish populations from lakes, mainly brown trout (*Salmo trutta*) (Hesthagen, Sevaldrud, & Berger, 1999). During the last 25 years, great efforts have been made to improve acidified waters by liming in Norwegian waters (Sandøy & Romundstad, 1995). Effects of liming on both crustaceans and fish have been studied in acidified areas in both Scandinavia and North America (Keller, Gunn, & Yan, 1992;

T. Hesthagen (✉)
Norwegian Institute for Nature Research,
Tungasletta 2, N-7485 Trondheim, Norway
e-mail: trygve.hesthagen@nina.no

B. Walseng
Norwegian Institute for Nature Research,
Gaustadalléen 21, N-0349 Oslo, Norway

L. R. Karlsen
Østfold County Council, Environmental Administration,
P. O. Box 325, N-1502 Moss, Norway

R. M. Langåker
Directorate for Nature Management,
Tungasletta 2, 7485 Trondheim, Norway

Degerman, Henrikson, Hermann, & Nyberg, 1995, Walseng, Raddum, & Kroglund, 1995; Yan, Keller, Somers, Pawson, & Girard, 1996; Appelberg, 1998). In Norway, crustaceans show strong signs of recovery 10–15 years after liming (Walseng, Raddum, & Kroglund, 1995; Walseng & Karlsen, 2001). For fish, damaged populations of the most common species, e.g. brown trout and perch (*Perca fluviatilis*) have recovered rapidly after liming (Forseth et al., 1997; Kleiven & Håvardstun, 1997; Hesthagen & Saksgård, 2000). However, little is known about to which extent lost populations may re-colonize limed lakes.

This study examined the recovery of fish and crustaceans in acidic, weakly acidic and limed lakes in River Enningdal watershed in southeastern Norway. This area was selected because of the high diversity of these two organism groups. The watershed was originally highly acidified, as several lakes prior to liming had pH of between 4.5 and 4.8 (Raddum, Hagenlund, & Halvorsen, 1984; Vasshaug, 1990). In this watershed fish and invertebrates have suffered from acidification for several decades, probably since the 1930s (Almer, 1972). Liming started in the early 1978s, and during this decade all larger lakes were treated. We hypothesized that water quality has been relatively stable since liming started, and species composition and communities should now be dominated by species normally associated with circum-neutral lakes.

2 Study Area

The River Enningdal watershed covers an area of 780 km² which is shared between Norway (1/3) and Sweden (2/3), and includes 61 lakes ≥ 1.0 ha in Norway (Fig. 1). The watershed has its sources in Lake Nordre Boksjo, which is situated in the northern part of the watershed. From this lake the main river runs southwards through the lakes Søndre Boksjo, Nordre and Søndre Kornsjø and Bullaresjön in Sweden. From the outlet of Lake Bullaresjön, River Enningdalselva turns 180° and flows northwards and back into Norway. The marine limit is located at 174 m above the present sea level, and lakes located above this altitude are more acidic and aluminium-rich than lakes situated below, as these are affected by marine sediments. The study lakes are situated between 17 and 230 m above sea level, with surface

areas between 1.0 and 812.8 ha. Twenty six of the lakes (43%) are now either limed or affected by liming, covering 93% of the total lake area. On a larger scale, liming started in 1980 when Lake Søndre Boksjo was treated, and several lakes have been limed on an annual basis since the mid 1980s.

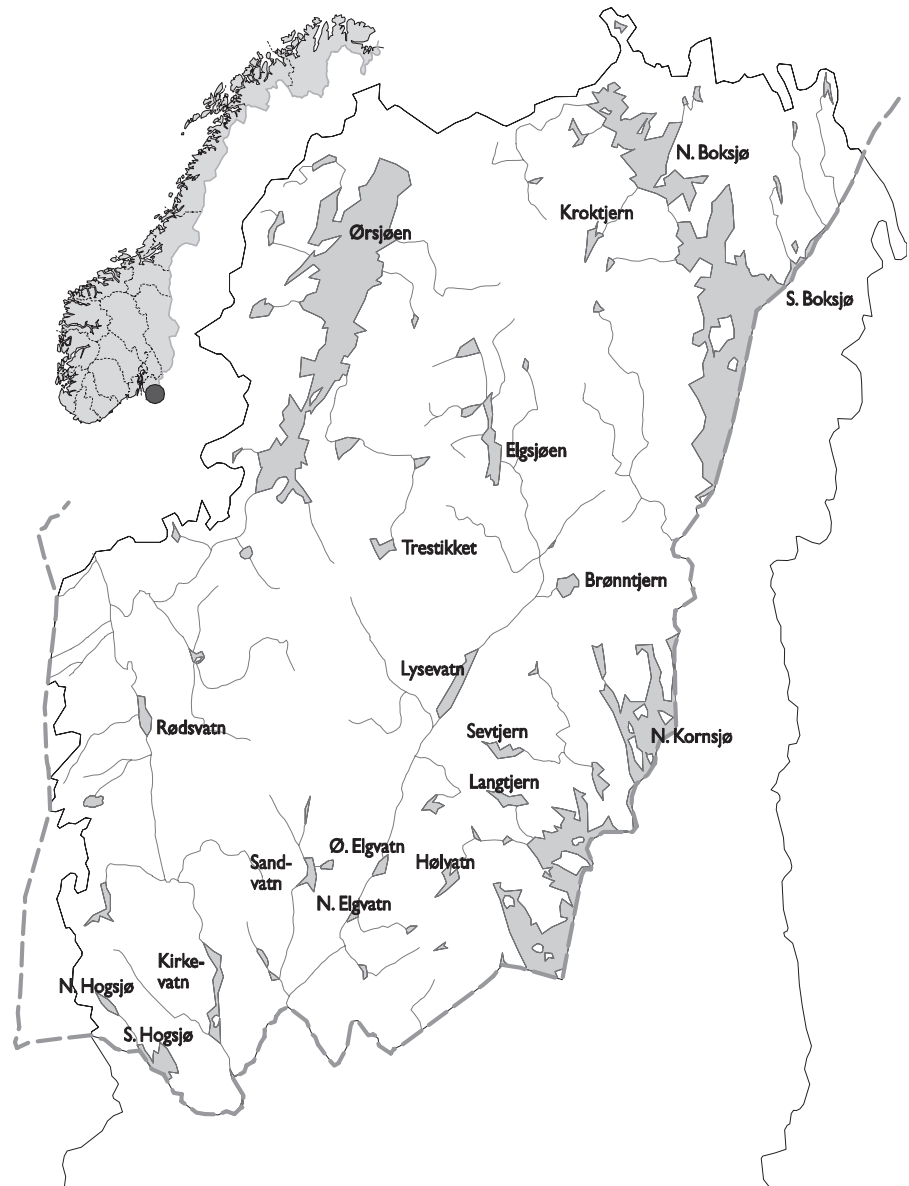
3 Materials and Methods

Analysis of water quality, sampling of crustaceans (copepods and cladocerans) and test-fishing were conducted in 24 lakes during a three-year-period (2002–2004). Water was sampled in each lake in August, and the samples were stored at low temperatures until they were analyzed within a few days, based on standard methods (Hesthagen, Heggenes, Larsen, Bergen, & Forseth, 1999). We used a Radiometer model PHM 84 pH meter with separate glass and reference electrodes to measure pH. Aluminium (Al) fractions were measured by means of a FIA Star model 5020, using the pyrocatechol violet method (Dogan & Wilson, 1974). Inorganic monomeric Al (Al-L) was calculated from total monomeric Al – organic monomeric Al. Acid neutralizing capacity (ANC) was estimated as the sum of all basic cations (BC) – sum of all the strong acid anions [SAA]. Crustaceans were collected both at the end of June and end of August, while testing-fishing was carried out in the last period. Fifteen of the study lakes are limed (Table 1). Of the non-treated lakes, six are highly acidic, of which five are situated above the old marine line, while three lakes are less affected by acidification. Lakes in the latter category are all situated below the formerly marine line, with rich geology and aggregation of marine sediments. All limed lakes have been severely affected by acidification.

Altogether 192 qualitative crustacean samples have been analysed. Samples were taken by a 30 cm diameter, 90 μ m mesh net haul from the deepest part of the lake (planktonic) and from the most frequent habitat in the littoral zone (one on stony substrate and one on stands of vegetation in each lake). Samples were preserved in diluted formaldehyde (4%). In general, entire samples were counted, but when >400 organisms were present, successive 10 ml subsamples were examined until at least 200 organisms were counted.

Test-fishing was carried out by using Nordic multi-mesh gill nets (30 m long and 1.5 m deep), with 12

Fig. 1 Location and outline of the Norwegian part of Enningdal watershed with identification of the largest lakes



different mesh sizes between 5–55 mm (Appelberg et al., 1995). We conducted stratified sampling at standard depth intervals of 0–3, 3–6, 6–12 and 12–20 m. The nets were left overnight for about 12 h periods. In addition, floating nets were used in the largest lakes (10–45 mm mesh size). Information from land owners and local fishermen was used to construct the historical fish community status for lakes in Enningdal watershed (Hesthagen, Rosseland, Berger, & Larsen, 1993). Such data have been obtained in different periods: (a) the 1950s (Vasshaug, 1990), (b) in the 1970s, 1980s and 1990s (Sevaldrud & Muniz,

1980; Hesthagen, Heggenes et al., 1999; Hesthagen, Sevaldrud et al., 1999) and (c) in 2001–2004 (present study). Fish status data were obtained for 44 of 61 lakes > 1.0 ha, of which three lakes were reported to never have supported fish. The remaining lakes ($n=17$) are small (0.2–1.0 ha), and most of them have probably always been empty of fish.

A species and site data matrix from the years 2002–2004 (24 lakes) based on recordings of presence/absence of fish and crustaceans were used as input in a multivariate analysis. Patterns in the distributions of crustaceans for the different sites were

Table 1 Altitude and lake area and some chemical factors: pH, alkalinity (ALK), calcium (Ca), labile aluminium (Al-L) and acid neutralizing capacity (ANC) for sampled lakes in Enningdal watershed

Locality	Altitude (m)	Area (ha)	Water quality status	pH	ALK $\mu\text{ekv l}^{-1}$	Ca mg l^{-1}	Al-L $\mu\text{g l}^{-1}$	ANC $\mu\text{eq l}^{-1}$
Blanktjern	206	1.9	Acid, not limed	4.90	0	0.90	53	11
Danmarktj	128	4.7	Weakly acid, not limed	5.72	51	2.44	8	92
Morttjern	230	1.0	Acid, not limed	5.09	0	1.07	57	-9
Kornsjø N*	141	552.3	Limed	6.87	224	5.56	0	232
Haugåstj St	182	6.7	Acid, not limed	5.09	0	0.85	74	3
Boksjø S*	166	812.8	Limed	7.06	221	5.89	4	229
Trestikket	214	11.0	Acid, not limed	5.12	0	0.45	42	-5
Ørsjøen	142	635.1	Limed	6.47	66	2.60	4	75
Hauganetj	132	9.9	Limed	5.80	45	1.89	10	112
Ellefsrødtj	150	12.2	Limed	6.45	77	3.29	4	123
Løksvatn	142	12.4	Weakly acid, not limed	5.49	33	1.74	21	123
Lysevatn	132	29.6	Limed	6.64	140	3.89	1	217
Elgvatn Ø	112	7.3	Limed	6.05	63	2.21	4	153
Langtjern	146	13.8	Limed	6.47	75	2.07	1	130
Boksjø N	173	204.5	Limed	6.61	92	3.03	1	99
Kroktjern	230	10.7	Acid, not limed	4.80	0	0.75	33	2
Rødsvatn	17	14.5	Limed	6.90	144	3.45	0	138
Hogsjø S	107	29.9	Limed	7.27	225	5.12	9	215
Godavatn	141	2.8	Weakly acid, not limed	6.03	50	1.44	15	68
Hokksjø	148	11.9	Acid, not limed	5.22	11	0.86	38	14
Elgsjøen	168	34.7	Limed	6.41	75	2.48	0	92
Geddelundj	179	10.9	Limed	6.45	60	2.13	0	79
Brønntjern	154	14.0	Limed	6.59	105	2.61	0	127
Kirkevatn	37	31.6	Limed	6.90	142	3.42	0	147

*Lake area in Sweden not included.

summarised by Detrended Correspondence Analysis (DCA), using the program CANOCO with down-weighting of rare species. The ordination results are presented in a diagram where the sites are represented by points along axes in a two-dimensional space. The diagram is a graphical summary of the data, and the axes can be interpreted as underlying environmental gradients. Sites which are geographically close correspond to sites which are similar in species composition. Sites which are far apart correspond to sites which are dissimilar in species composition.

4 Results

4.1 Water Quality

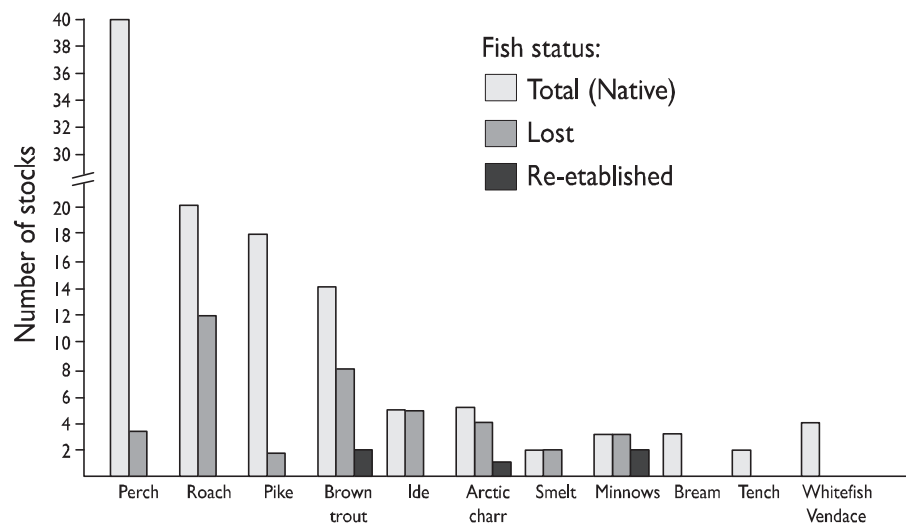
Among the lakes sampled to measure water quality ($n=24$), pH, Ca, labile Al (Al-L) and acid neutralising capacity (ANC) varied between 4.80–7.27, 0.45–5.89 mg l^{-1} , 0–74 $\mu\text{g l}^{-1}$ and -9 to + 232 $\mu\text{eq l}^{-1}$,

respectively (Table 1). The mean value $\pm$ S.D. of pH and Al-L in the six acidic, non-limed lakes were 5.0 ± 0.14 and $52 \pm 16 \mu\text{g l}^{-1}$, respectively. The remaining non-limed lakes, being situated below the formerly marine line, had higher pH (5.74 ± 0.47) and much lower Al-L ($16 \pm 14 \mu\text{g l}^{-1}$). Liming has highly detoxified the water, with nearly neutral pH (6.62 ± 0.35) and almost no Al-L ($3 \pm 4 \mu\text{g l}^{-1}$).

4.2 Fish Communities

A total of 14 different fish species either exist or have previously existed in lakes from which fish status were obtained ($n=41$) (Fig. 2). The mean number $\pm$ S. D. of fish species prior to acidification in lakes with fish was 2.9 ± 2.0 as opposed to 1.9 ± 1.3 at present. Originally, these lakes supported at least 120 populations of fish, of which 42 (35%) have gone extinct. Perch is now the dominant species, followed by pike (*Esox lucius*) and roach (*Rutilus rutilus*). Perch was the only species in 37% ($n=15$) of lakes containing

Fig. 2 The total number of different species of fish in lakes in Enningdal watershed, with number of lost and re-established populations



fish. Roach has suffered the largest damage as 12 of 20 populations (60%) have been lost. Only five (12%) of the lost fish populations have been re-established after liming. This is due to introductions by man, either from stockings programmes such as for brown trout and Arctic charr (*Salvelinus alpinus*), or by accidental introduction of European minnow (*Phoxinus phoxinus*).

4.3 Crustaceans

A total of 71 crustacean species (50 cladocerans and 21 copepods) were recorded between 2002 and 2004. Five cladoceran species (*D. brachyurum*, *B. longispina*, *A. harpae*, *A. affinis* and *P. pediculus*) and the copepod *Macrocyclus albidus* were identified in all lakes. The number of species varied from 20 in one of the acidic lakes to 47 in Lake Kirkevatn which was limed. The mean number $\pm$ S.D. of crustaceans in acidic, weakly acidic and limed lakes were 23.2 ± 2.0 , 36.3 ± 4.7 and 35.8 ± 4.5 , respectively.

4.4 DCA-ordination

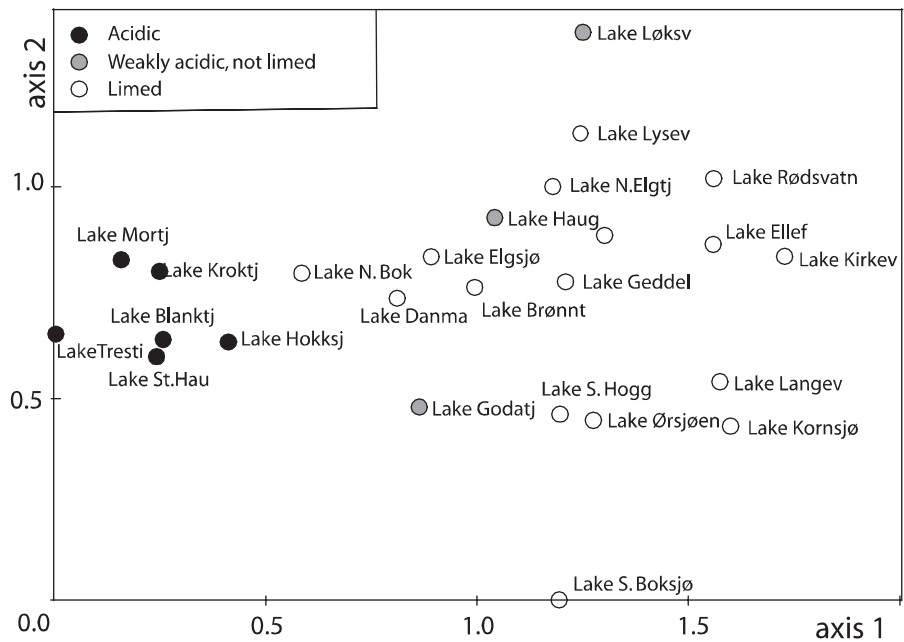
When absence/presence data including fish and crustaceans were used as input in an ordination analysis (DCA) (24 lakes, 82 species), a site data matrix showed that plots representing the most acidic lakes were grouped at the left end of axis 1 whereas plots representing near neutral lakes were grouped at the opposite end (Fig. 3). The length of axis 1 was

1.73 S.D. units, explaining 23% of the total variance in the dataset. When crustaceans were analysed separately, the new plot diverged only slightly from the former one. The length of axis 1 was 1.72 S.D., explaining 24% of the total variance in the dataset. A DCA-ordination of fish-species reflected that perch occurred in all lakes and that the position of some of the near neutral lakes was determined by species that were unique for actual the lake.

Six acidic, non-limed lakes were found in the left end of axis 1 while five limed lakes (Rødsvatn, Kirkevatn, Ellefsrødtjern, Langtjern and Nordre Kornsjø) were situated at the opposite end (Fig. 3). The correlation between axis 1 and pH was highly significant ($r^2=0.55$, $P<0.001$). Acid tolerant crustaceans like *Acantholeberis curvirostris* and *Diacyclops nanus* were associated with acid lakes, while the cladocerans *Limnospina frontosa*, *Ceriodaphnia pulchella*, *Daphnia cristata*, *Bosmina longirostris*, *Ophryoxis gracilis*, *Alona costata*, *Alonella exigua* and *Disparalona rostrata*, and the copepods *Heterocope appendiculata*, *Eucyclops macrurus* and *E. speratus* were associated with the neutral lakes. There were no fish species associated with the acidic lakes only. Perch, which is found in acidic lakes, also occurs in the remaining lakes and has a central position in the species plot.

The number of species increases with pH. As a consequence of the relation between pH and species composition, parameters that correlate to pH are also correlated to axis 1. Alkalinity ($r^2=0.56$, $P<0.001$), Ca ($r^2=0.50$, $P<0.01$), Mg ($r^2=0.57$, $P<0.001$),

Fig. 3 DCA-ordination sample plot based on fish and crustacean species (absence/presence) found in acidic, weakly acidic (not limed) and limed lakes in Enningdal watershed, 2002–2004



K ($r^2=0.47$, $P<0.01$) and labile Al ($r^2=-0.55$, $P<0.001$) are such examples, which is also confirmed by using conductivity as a measure representing electrolytes ($r^2=0.62$, $P<0.001$). Axis 2 was correlated to both water colour or the humic content of the lake ($r^2=0.38$, $P<0.05$), and to total Al ($r^2=0.37$, $P<0.05$). *Ceriodaphnia quadrangula*, *Graptoleberis testudinaria*, *Iliocryptus sordidus* and *Alona costata* were associated with the humic lakes, while *Rhynchotalona falcata* and *Eucyclops macrurus* are common in clear water lakes.

5 Discussion

Lakes in Enningdal watershed in southeastern Norway were highly acidified before large-scale liming was initiated in the 1980s. We show that liming has detoxified the water, as indicated from pH and concentration of labile Al. Fish has so far failed to respond positively to this improved water quality in terms of re-establishing natural fauna. Of a total of 42 lost fish populations, only five populations (12%) have recovered, all due to human introductions. The low rate of fish recovery in limed lakes the watershed is considered to be due to physical barriers between the different lakes, preventing them from invading these lakes with acceptable water quality. Thus, in order to re-establish the original fish fauna

in limed lakes, large re-stocking efforts seems to be necessary. Recolonization of fish species in limed Swedish lakes was also found to be a crucial factor for the development of fish assemblages after treatment (Appelberg, 1998).

Acidification has impoverished the fish fauna in Enningdal as water quality deterioration wiped out several species sensitive to acidification, such as brown trout and roach. Perch is more tolerant of acidification than the former species, and today 37% of the lakes with fish have only perch. This species has also developed dense populations in most of the limed lakes. Also in limed Swedish lakes, the relative biomass of perch was general higher than in the non-limed circumneutral lakes (Appelberg, 1998).

Planktonic and littoral crustaceans have responded to a greater extent than fish to improved water quality due to liming. Some of the limed lakes contained more than twice as many crustacean species as the non-limed acidic lakes. Our hypothesis was that the lakes would reflect most of the species variation along a pH gradient though DCA analysis showed that limed and the weakly acidic lakes were at the opposite end of the acidic lakes. Samples were not taken before the lakes were limed, but considering that pH in some of these lakes was <5.0 before liming, it seems obvious that improved water quality has resulted in the increased diversity of crustaceans. Acid-tolerant species were associated with acidic

lakes, while acid-sensitive species dominated the weakly acidic and limed lakes.

Increased zooplankton diversity due to improved water quality had earlier been documented in Canada (Yan et al., 1996), Sweden (Degerman et al., 1995) and different areas of Norway (Walseng et al., 1995). Studies from Norway have also shown recovery among littoral crustaceans (Walseng & Karlsen, 2001; Walseng, Halvorsen, & Sloreid, 2001). Recovery of crustaceans within the Enningdal watershed was therefore expected. An increase in species number is caused by re-establishment of acid sensitive species which did not survive during the highly acidified periods. This is mainly due to their good spreading capacity, as small organisms like algae and crustaceans can be transferred passively by wind or be attached to different objects that are moved (Maquire, 1963; Proctor, 1964; Brendonck & Riddoch, 1999). Some crustaceans species may also have survived in refuges within the watershed during acidification, where the water quality remain satisfactory such as in lakes which are located below the formerly marine line. Some species like *Daphnia* sp. may also survive for many years as resting-eggs in the sediment (Weider, Lampert, Wessels, Colbourne, & Limburgh, 1997).

References

- Almer, B. (1972). *Information from the Institute of Freshwater Research Drottningholm*. No 12. 47 pages.
- Appelberg, M. (1998). *Restoration Ecology*, 6, 343.
- Appelberg, M., Berger, H. M., Hesthagen, T., Kleiven, E., Kurkilahti, M., Raitaniemi, J., et al. (1995). *Water, Air and Soil Pollution*, 85, 401.
- Brendonck, L., & Riddoch, B. J. (1999). *Journal of the Linnean Society*, 67, 87.
- Degerman, E., Henrikson, L., Herrmann, J., & Nyberg, P. (1995). The effects of liming on aquatic fauna. In L. Henrikson & Y. W. Brodin (Eds.), *Liming of acidified surface waters. A Swedish synthesis* (pp. 221–282). Berlin Heidelberg New York: Springer.
- Dougan, W. K., & Wilson, A. L. (1974). *Analyst*, 99, 413.
- Forseth, T., Halvorsen, G. A., Ugedal, O., Fleming, I., Schartau, A. K. L., Nøst, T., et al. (1997). Norwegian Institute for Nature Research, Trondheim, *NINA-Oppdragsmelding* 508, 52 pages. (In Norwegian with summary in English).
- Hesthagen, T., Rosseland, B. O., Berger, H. M., & Larsen, B. M. (1993). *Nordic Journal of Freshwater Research*, 68, 34.
- Hesthagen, T., Heggenes, J., Larsen, B. M., Berger, H. M., & Forseth, T. (1999). *Water, Air and Soil Pollution*, 112, 85.
- Hesthagen, T., & Saksgård, R. (2000). Norwegian Institute for Nature Research, Trondheim, *NINA-Oppdragsmelding* 643, 18 pages. (In Norwegian with summary in English).
- Hesthagen, T., Sevaldrud, I. H., & Berger, H. M. (1999). *Ambio*, 28, 12.
- Keller, W., Gunn, J. M., & Yan, N. D. (1992). *Environmental Pollution*, 78, 79.
- Kleiven, E., & Håvardstun, J. (1997). Norwegian Institute for water Research, Oslo, *NIVA-Report* 3765–97, 174 pages. (In Norwegian with summary in English).
- Maquire, B., Jr. (1963). *Ecological Monographs*, 33(2), 161.
- Proctor, V. W. (1964). *Ecology*, 45(3), 656.
- Raddum, G. G., Hagenlund, G., & Halvorsen, G. A. (1984). *Report from the Institute Freshwater Research Drottningholm*, 61, 167.
- Sandøy, S., & Romunstad, A. J. (1995). *Water, Air and Soil Pollution*, 85, 997.
- Schindler, D. W., Frost, T. M., Mills, K. H., Chang, P. S. S., Davies, I. J., Findlay, D. L., et al. (1991). *Proceedings of the Royal Society Edinburgh*, 97B, 193.
- Sevaldrud, I. H., & Muniz, I. P. (1980). *Impact of Acid Precipitation*, SNSF project, Internal Report 77/80. 95 pages. (In Norwegian with summary in English).
- Vasshaug, J. (1990). Fylkesmannen i Østfold, Miljøvernnavd., Report 14–1990, 84 pages. (In Norwegian).
- Walseng, B., Halvorsen, G., & Sloreid, S. E. (2001). *Hydrobiologia*, 450, 159.
- Walseng, B., & Karlsen, L. R. (2001). *Water, Air and Soil Pollution*, 130, 1313.
- Walseng, B., Raddum G. G., & Kroglund, F. (1995). DN-utredning 1995–6, 63 pages. (In Norwegian).
- Weider, L. J., Lampert, W., Wessels, M., Colbourne, J. K., & Limburgh, P. (1997). *Proceedings of the Royal Society of London Series. Biological Sciences*, 264(1388), 1613.
- Yan, N. D., Keller, W., Somers, K. W., Pawson, T. W., & Girard, R. E. (1996). *Canadian Journal of Fisheries and Aquatic Sciences*, 53, 1301.

Recovery of Acidified Streams in Forests Treated by Total Catchment Liming

Olle Westling · Therese Zetterberg

Received: 17 June 2005 / Accepted: 27 March 2006 / Published online: 6 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Reduced emissions of acidifying pollutants have changed the acidification process, and as a result, forest soils and surface waters are slowly recovering in Sweden. However, model calculations show that some areas may never recover completely unless further measures, such as liming, are undertaken. Liming of surface waters (lakes, rivers and wetlands) has been successfully practised in Sweden since the 1970s, but repeated treatments are necessary. A full recovery of acidified lakes and streams without frequent liming is however not possible until soil acidification is reversed in the most strongly affected areas. In this study, the recovery of acidified streams was examined using ‘the total catchment approach’ i.e. treatment of both recharge and discharge areas. The aim was to compare the quantitative effect of different treatments on run off chemistry and the recovery of brown trout. Catchments in southwest Sweden were treated with a combination of 2 tons of wood ash and 4, 6 or 12 tons of crushed limestone per hectare in 1998/1999. Treatment of both recharge and discharge areas resulted in fast and significant changes in stream water quality, e.g. increased concentrations of calcium, higher pH and ANC and a decreased

concentration of inorganic aluminium. The initial changes were dependent on the distribution of the applied lime between discharge and recharge areas rather than the average dose on the total catchment. Treatment of recharge areas only, resulted in smaller but still significant effects on calcium, pH and ANC in stream water. Furthermore, there was an initial leaching of nitrate but it was only minor compared with the elevated leaching that occurs after a clear-cut. As a result of the treatments, brown trout is now successfully reproducing.

Keywords acidification · ANC · brown trout · catchment · discharge · forest soil · inorganic Al · limestone · wetland · wood ash

1 Introduction

Atmospheric deposition of sulphur and nitrogen during the last century has caused severe acidification of surface waters and forest soils in Sweden, especially in the southwestern parts. For instance, pH has declined by more than a unit and base saturation has decreased by 30–50% in deep soil horizons during the last 30–50 years (Falkengren-Grerup, Linnermark, & Tyler, 1987). Joint European efforts have reduced emissions of acidifying pollutants, and as a result, deposition of SO₂ has decreased by approximately 50% and NO_x by 30% in Sweden during the 1990s (Lövblad et al., 2004). Forest soil and surface water inventories show

Olle Westling (deceased).

O. Westling · T. Zetterberg (✉)
IVL Swedish Environmental Research Institute,
P.O. Box 5302, 400 14 Gothenburg, Sweden
e-mail: therese.zetterberg@ivl.se

clear signs of recovery from acidification as a result of the emission reductions (Wilander & Lundin, 2000). However, model calculations show that it may take decades or even centuries for some areas to fully recover unless further reductions are undertaken (Sverdrup et al., 2005). The acidification situation is also made worse by the use of biofuels from forests. Harvesting of logging residues may lower the use of fossil fuels but on the other hand removes valuable and buffering nutrients from the forest, unless wood ash is returned (Olsson, Rosén, & Melkerud, 1993). As biofuels are becoming an important source of energy in Sweden (The National Board of Forestry, 2005) it is more important than ever to take action into preventing further acidification.

Liming of surface waters (lakes, rivers and/or wetlands) has proved to be successful in restoring the quality of water and biological habitats of fish populations in rivers and lakes, and the method is widely used in the Swedish acid rain mitigation program (Dickson & Brodin, 1995). However, in order to sustain the effect, liming needs to be repeated once every few years (at a governmental cost of 22 millions Euro per year) or to be combined with forest soil treatment. A full recovery of acidified lakes and streams is not possible until soil acidification is reversed.

The aim of this study was to compare the quantitative effect of different treatments on stream water chemistry using a total catchment approach. The goal of the treatments is to reduce the leaching of inorganic aluminium to surrounding waters and restore the biological habitat of brown trout (*Salmo trutta*) without any negative side effects. The hypothesis was that liming and wood ash application on recharge areas will gradually and long lasting increase base saturation and reduce aluminium leaching, while liming of discharge areas will give a quick but decreasing neutralising effect on run off water, (Fig. 1). Figure 1 shows, in a schematically way, that natural recovery has begun, but run off water will not reach the critical concentration of ANC unless further measures are undertaken.

2 Materials and Methods

2.1 Site Description

The research area is situated in the southwest parts of Sweden, 30 km northeast of Halmstad in the county

of Halland near the village of Fröslida (Fig. 2). It is located 80–175 meters above sea level and is dominated by coniferous forest (*Picea abies*) with smaller populations of beech (*Fagus sylvatica*), birch (*Betula pubescens* and *Betula pendula*) and alder (*Alnus glutinosa*) found in scatters and along the margins. The mineral soil consists of glacial till onto which podzols have developed. Peat formation can be found in smaller areas where pine (*Pinus sylvestris*) grows. The area has previously experienced high deposition of sulphur that has now decreased, but the deposition of nitrogen continues to be high.

The research area is divided into six catchments of which one (catchment 2) contains six subcatchments also included in this study (Fig. 2). In the following text the subcatchments will be referred to as catchments. There are two major catchments areas (No. 2, circa 300 ha, and No. 4, 200 ha) while the remaining areas vary between 5 and 46 ha. The total area of each catchment can be found in Table 1, with a distinction between recharge and discharge areas. Discharge areas, defined as fens with or without trees, were identified by aerial photos and by field inventories. An extensive site description (both in Swedish) can be found in Larsson, Westling, and Abrahamsson (2003) and Wickström et al. (2004).

2.2 Treatments

Eight of the twelve catchments were treated with wood ash and different doses of crushed limestone between November/December 1998 and April/May 1999, while the remaining four catchments were untreated and hence used as references. Wood ash is a by-product from burning biofuels such as logging residues in heating plants. Compared with limestone,

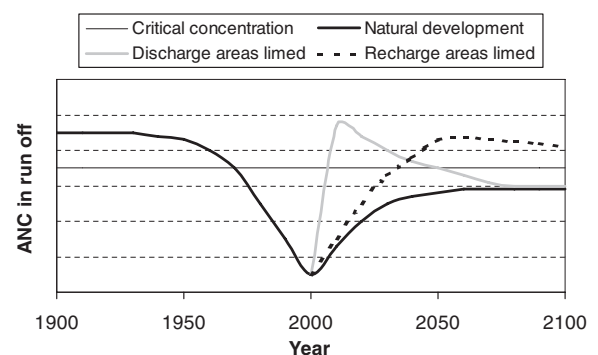
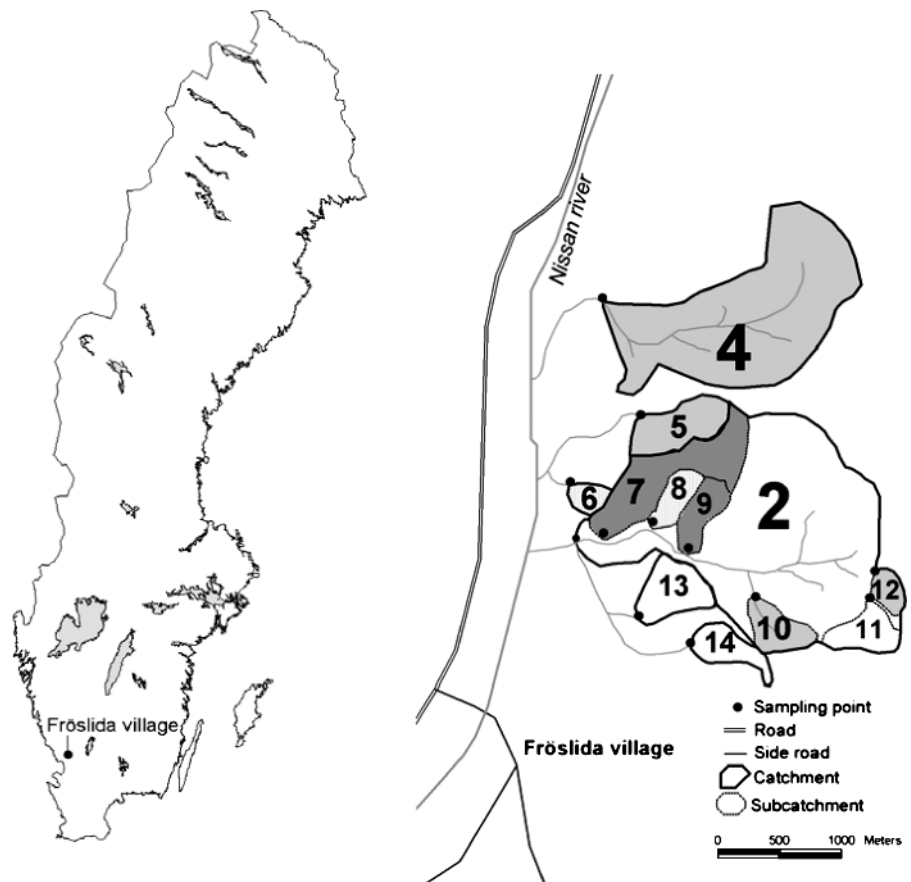


Fig. 1 The concept of total catchment liming in theory

Fig. 2 Location of the research area, near Fröslida village. The area is divided into six catchments (2, 4, 5, 6, 13 and 14) and six sub-catchments (7, 8, 9, 10, 11 and 12)



wood ash contains all nutrients originally found in the tree, apart from nitrogen.

Initially a helicopter was used but due to technical problems a tractor completed the remaining treatments in spring of 1999. The catchments were divided into

four different categories depending on the treatment. In category one (catchment 6 and 8), only recharge areas were treated with a base dose of 2 tons of wood ash and 4 tons of crushed limestone. In category two (catchments 2, 11, 13 and 14) both recharge and discharge

Table 1 The total area of the catchments with a distinction between recharge and discharge areas and the doses applied

Catchment	Total area Size (ha)	Discharge area		Recharge area	
		Total dose (ton/ha)	Size (ha)	Total dose (ton/ha)	Size (ha)
2	312	3.8	13.7	10.6	298.3
4	200	—	—	—	—
5	20	—	—	—	—
6	4.6	7.7	0	—	4.6
7	46	6.5	4.7	16	41.3
8	7	5.8	0	—	7
9	9	5.1	1.1	11.7	7.9
10	10	—	—	—	—
11	18	4.9	0.4	6	17.6
12	5	—	—	—	—
13	20	5.3	2.7	5.3	17.3
14	14	6.1	1.3	6.1	12.7

areas were treated with the base dose. In category three (catchments 7 and 9) recharge and discharge areas were treated with the base dose while the discharge areas also received an extra dose of crushed limestone of either 6 (catchment 9) or 12 (catchment 7) tons per hectare. Finally, in category four, catchments 4, 5, 10 and 12 were left untreated and used as reference areas. A summary of the doses applied can be found in Table 1. Notice minor differences between applied and planned dose in some cases.

2.3 Analysis and Statistics

Run off water was collected on a monthly basis by means of a plastic bottle, and analysed with respect to pH, alkalinity, conductivity, colour, sulphate ($\text{SO}_4\text{-S}$), chloride (Cl^-), nitrate ($\text{NO}_3\text{-N}$), total nitrogen (Kjeldal-N), total phosphorous (total-P), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), iron (Fe^{2+} and Fe^{3+}), manganese (Mn^{2+}), total aluminium (total-Al) and organic aluminium (org-Al). Chemical analysis was carried out by standard accredited methods apart from Mn^{2+} , which was analysed using an ion chromatography. Individual samples were grouped according to the four categories of treatments and presented as average concentrations on a monthly or yearly basis.

Monthly averages of concentrations of Ca^{2+} , ANC, pH and inorganic Al from the three groups of treatments were tested against the reference group using a dependent *t*-test for the period June 1999–October 2004. $\text{NO}_3\text{-N}$ was only tested against reference catchments 4, 5 and 10 since an area of 1.3 ha in reference area 12 was clear-cut in October 1999, which increased the leaching of nitrate. Furthermore, the test was divided into two periods, June 1999–May 2000 and June 2000–October 2004 in order to show the short- and long-term effects on nitrate leaching.

2.4 Sampling of Brown Trout

The occurrence of brown trout was studied in two streams (Skärsjöbäcken and Krokabäcken) using electric fishing gear prior to, and after treatment. The streams are located in the two major catchments (No. 2 and No. 4). Both streams were examined between 1998–2000 and Skärsjöbäcken was examined again between 2002–2005 and Krokabäcken in 2004.

3 Results

3.1 Water Chemistry

In general, changes in stream water quality were more significant, and occurred at an earlier stage downstream catchments where both recharge and discharge areas were treated compared with catchments where only recharge areas were treated. A summary of the effects is presented in Table 2.

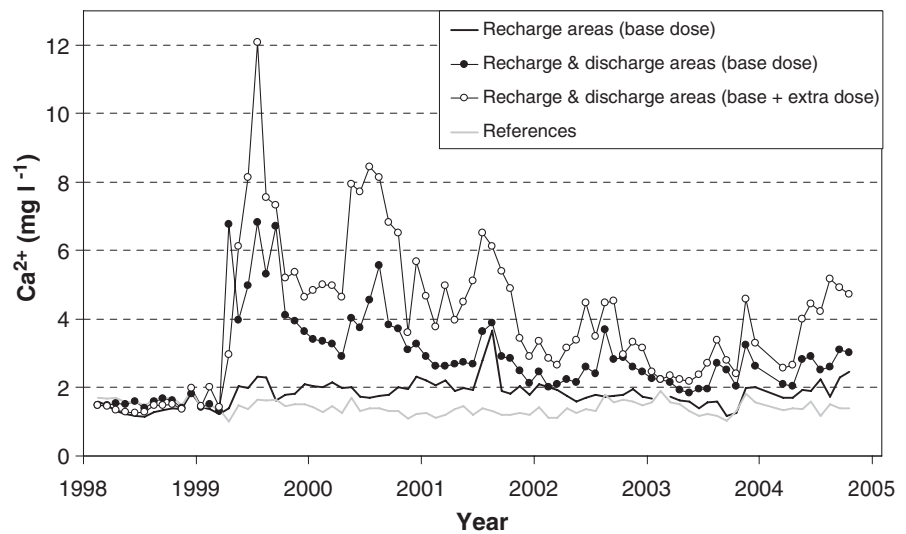
The concentration of Ca^{2+} in run off water from areas where both recharge and discharge areas were treated with a base or extra dose increased rapidly immediately after application, as shown in Fig. 3. This effect declined after two to three years at a lower but still elevated level. Ca^{2+} -concentrations also increased in base dose treated recharge areas, but the increase was not to the same magnitude. Seasonal variations in Ca^{2+} were also evident, with higher concentrations in summertime due to reduced amounts of run off water making water more concentrated. Consequently, wintertime was characterised by lower Ca^{2+} concentration values due to increased levels of run off.

The pH in run off water was close to 4.2 in all areas prior to treatment as shown in Fig. 4. However, immediately after treatment, pH increased in all

Table 2 Result from the dependent *t*-test for the period June 1999–October 2004

Category	<i>P</i> -value					
	Ca^{2+}	ANC	pH	Inorganic Al	$\text{NO}_3\text{-N}$ (a)	$\text{NO}_3\text{-N}$ (b)
Recharge areas (base dose)	0.000 (↗)	0.000 (↗)	0.000 (↗)	0.367	0.000 (↗)	0.370
Recharge & discharge areas (base dose)	0.000 (↗)	0.000 (↗)	0.000 (↗)	0.000 (↘)	0.039 (↘)	0.057
Recharge & discharge areas (base+extra dose)	0.000 (↗)	0.000 (↗)	0.000 (↗)	0.000 (↘)	0.503	0.278

$\text{NO}_3\text{-N}$ (a)=June 1999–May 2003 and $\text{NO}_3\text{-N}$ (b)=June 2003–October 2004. The test has been performed to different categories of treatments rather than individual treatments. Arrows in brackets indicate the change, ↗=increase, ↘=decrease.

Fig. 3 Concentration of Ca^{2+} in run off water

treated areas compared with reference areas. Catchments where both recharge and discharge areas were treated showed a rapid and significant effect on pH while treatment of recharge areas only proved to have a slow, but delayed, response. Five and a half years after treatment the effect still remained and showed no sign of decline. In 2004, the pH in run off water from treated recharge areas was approximately 4.5 compared with treated recharge and discharge areas where pH was approximately 5.0.

As a consequence of elevated concentrations of Ca^{2+} (and Mg^{2+} and K^{+}), the acid neutralising capacity (ANC) also increased as shown in Fig. 5.

Treated recharge and discharge areas showed a quick and high response compared with treated recharge areas that received the base dose. Two years after treatment, ANC begun to decline in recharge and discharge treated areas. So far, ANC in run off water from treated recharge areas has increased slowly but steadily. Figure 5 also show a slow but natural recovery in the reference catchments. This behaviour is in accordance with the hypothesised conceptual behaviour as shown in Fig. 1.

Figure 6 show the concentration of inorganic aluminium, and already in the first year after treatment, significant changes could be found in run off

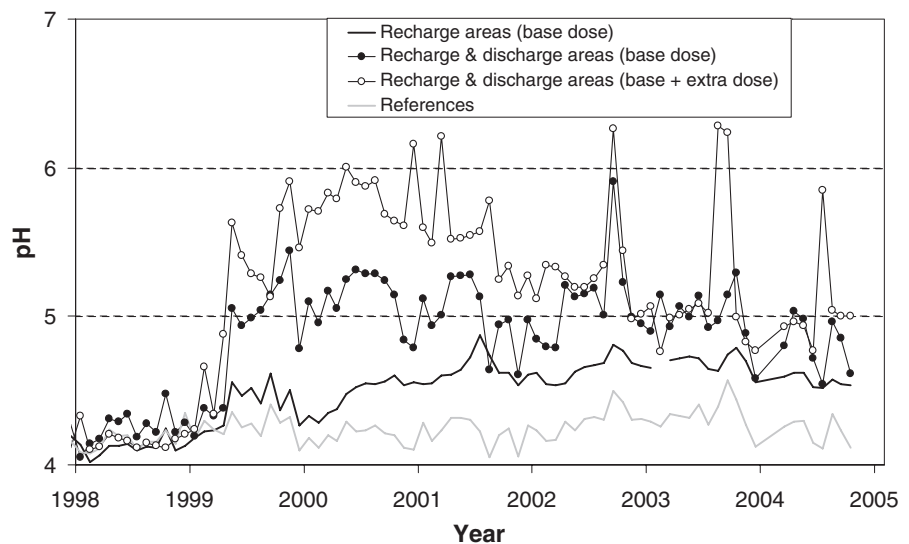
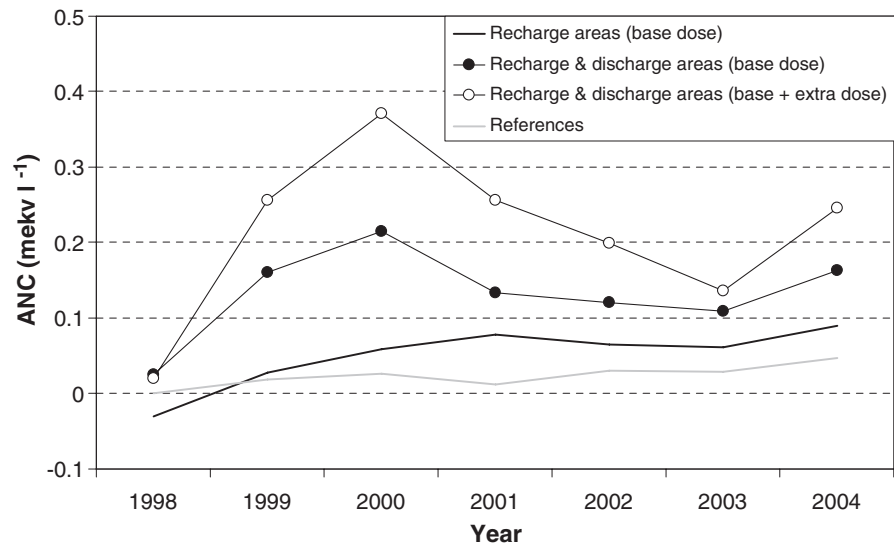
Fig. 4 pH in run off water

Fig. 5 Acid neutralising capacity (ANC) in run off water (yearly averages)



water from areas where both recharge and discharge areas were treated. So far, treatments of recharge areas have not had a significant effect on the concentration of inorganic aluminium.

Initially, nitrate concentration increased significantly in recharge areas treated with a base dose while the leaching significantly decreased in areas where both the recharge and discharge areas were treated with a base dose as shown in Fig. 7 and Table 2. This increase is however minor compared with the leaching that occurs after clear-cuttings (Akselsson, Westling, & Örlander, 2004), showed by the leaching in area 12 after a part of the catchment was clear-cut (Fig. 7). In comparison, no significant decrease could be found in run off water

from catchments where recharge and discharge areas were treated with an extra dose, but a decreasing tendency existed. Four years after treatment no difference could be found in nitrate concentration in run off between the treated catchments and the reference areas. Seasonal variations were evident with decreased leaching in summertime due to nutrient uptake and increased leaching in the winter when uptake is low.

The initial changes were dependent on the distribution of the applied lime between discharge and recharge areas (Fig. 8). The size of the discharge areas was of less importance. Catchments where both recharge and discharge areas were treated lowered

Fig. 6 Inorganic aluminium in run off water

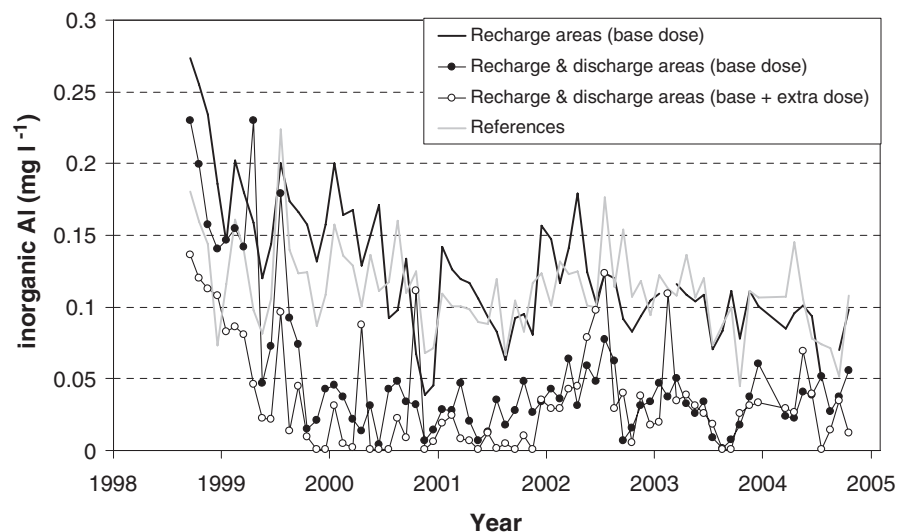
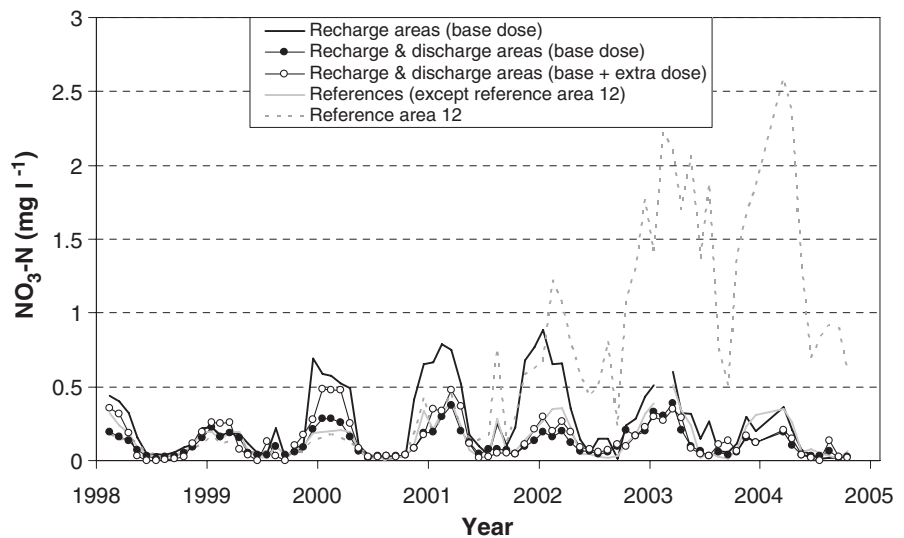


Fig. 7 Concentration of NO_3^- -N in run off water. A part of the reference area 12 was clear-cut October 1999, which increased the leaching



the concentration of inorganic aluminium in run off water regardless of the dose, with the exception of catchment 11 (Fig. 8). In contrast, ANC increased and the increase seemed to be related with the dose. Figure 8 also shows the variation between the different catchments.

3.2 Brown Trout

Brown trout have successfully started to reproduce in Skärsjöbäcken (Fig. 9) (catchment 2) for the first times in 40 years, according to local observations. Already in the same year of treatment, brown trout were spawning which resulted in spring-offs in the second year. As a

comparison, no brown trout could be found in Krokabäcken, located in the reference catchment.

4 Discussion

In this study a combination of both recharge and discharge treatments were applied. Liming and wood ash application resulted in significant improvements in stream water quality with increased concentrations of Ca^{2+} , higher pH and ANC regardless of the area treated. Furthermore, the amount of inorganic aluminium decreased significantly in run off water from catchments where both recharge

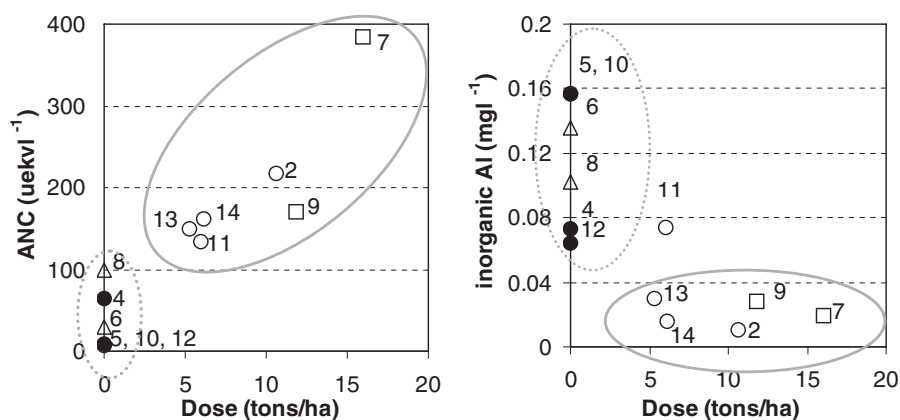
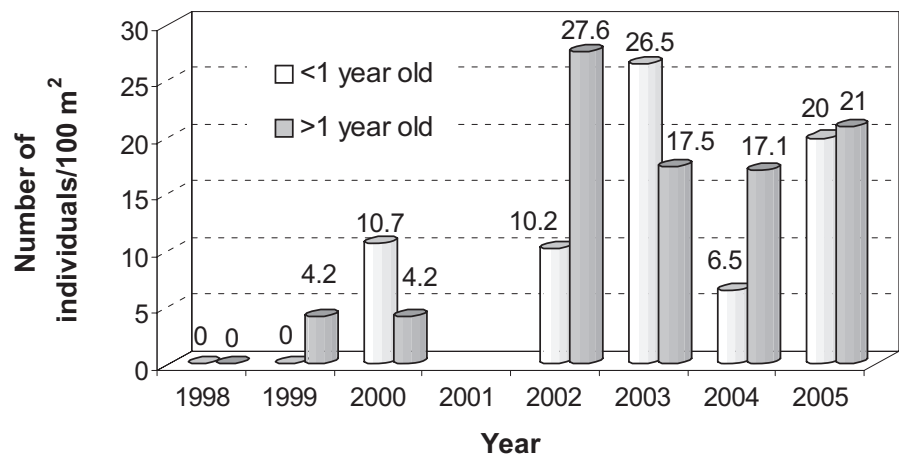


Fig. 8 Acid neutralising capacity (ANC) and inorganic aluminium in run off water as a function of total applied dose (wood ash and lime) on discharge areas. (Filled circle)=References, (open triangle)=recharge areas (base dose), (open circle)=recharge & discharge areas (base dose) and (open square)=recharge & discharge areas (base+extra dose). Volume weight

means for three hydrological years, October 1999 to September 2002. Shown in *large dashed circles* are treated recharge areas and references while *solid circles* represent areas where both recharge and discharge areas were treated with a base or extra dose

Fig. 9 The presence of brown trout in Skärsjöbäcken (catchment 2)



and discharge areas were treated, but have yet not decreased in run off water from catchments where only recharge areas were treated. This is in accordance with several other studies where positive effects on run off water have been reported after lime application on forest soils (Bell, 1992; Clair & Hindar, 2005; Direktoratet for naturforvaltning, 2001; Driscoll et al., 1996; Hindar, Wright, Nilsen, Larssen, & Hogberget, 2003; Larsson & Westling, 1997; Olem, 1991; Traaen et al., 1997; Westling & Hultberg, 1990) and wetlands (Borg, Ek, & Holm, 2001; Gunn, Sein, Keller, & Beckett, 2001).

The initial changes were dependent on the distribution of the applied lime between discharge and recharge areas rather than the average dose on the total catchment. One reason for the quick response in run off from water from catchments where both recharge and discharge areas were treated is a shorter residence time of subsurface water in discharge areas compare to recharge areas.

It is predicted that the concentration of inorganic aluminium will decrease in run off water from recharge areas with time as Ca^{2+} -ions are transported down the soil profile and pH and ANC increases. A review of eleven historical liming experiments in the southern and middle part of Sweden by Larsson, Uggla, and Westling (2003) showed that treatment of recharge areas significantly increased base saturation and acid neutralising capacity (ANC) in soil water, and possibly run off water, at 30–50 cm depth compared with references. Furthermore, the review indicated that the amount of inorganic Al was reduced. The prediction is further supported by Fransman and Nihlgård (1995) and Grieve (1990)

who was able to show decreasing concentrations of inorganic aluminium in stream waters as a result of increased soil ANC after forest soil liming.

As a result of liming and wood ash application, brown trout successfully started to reproduce during the second year of the experiment. The assessment is somewhat difficult to make due to the removal of a small obstruction in the summer of 1999, which cleared the way for brown trout to fully enter the stream. It is however unlikely that brown trout would have been able to reproduce pre-treatment, regardless of the obstruction, due to the acid- and aluminium-rich water. The absence of brown trout in the reference streams further supports this conclusion. The success of restoring fish habitats after catchment liming has been shown in several other studies (e.g. Baurlaup & Kleiven, 2004; Hindar & Wright, 2005; Traaen et al., 1997) and the effect may last for a long time. E.g. in Tjønnstad, Norway, stocked brown trout has been able to survive for more than 20 years after treatment with lime in 1983 (Traaen et al., 1997).

So far, the response in run off water from catchments where both discharge and recharge areas were treated supports the hypothesised conceptual theory presented in Fig. 1. The effects of discharge liming have culminated and the contribution from limed and ash-treated recharge areas is still limited due to the slow transport to deeper soil horizons. Further studies will show if the improved base saturation in catchments with a single treatment of recharge areas is sufficient to avoid acidification effects in the long run, when the effects of discharge liming have disappeared. If the deposition of acidifying air pollutants continues to decrease the prediction in this study is that the treatments of mineral

soils will have long term effects on preventing acidification of the run off. This is further supported in a review by Clair and Hindar (2005), who concluded terrestrial liming to be most effective and simplest mean to mitigate acidification.

In order for liming and wood ash application to be carried out it must take place without any negative side effects. There is a potential risk of nitrogen leaching to surrounding surface waters if the nitrification process is stimulated and excess nitrate is produced (Cirimo & Driscoll, 1996). Also, if the dynamics of the nitrogen cycle is changed the species composition of the field vegetation and tree growth might be affected (Andersson, Hallbäcken, & Popovic, 1996; Hallbäcken & Zhang, 1998). In the past, nitrogen leaching after liming has been observed in areas with high deposition of nitrogen or forest soils rich in nitrogen (Johansson, Nilsson, & Olsson, 1999). This increase seems to be temporary but there have been reports of increased concentrations 10 years after treatment (Huber, 1996). Leaching after wood ash application has not been observed (Fransman & Nihlgård, 1995). In this study, treatment of recharge areas resulted in an increased leaching of nitrate during the first four years. This increase was however temporary and not of the same magnitude as the leaching which occur after clear-cutting, (Akselsson et al., 2004). According to Löfgren and Westling (2002) the minimum concentration found in soil water after clear-cuts was estimated to 0.95 mg l^{-1} . In comparison, treatments of both recharge and discharge areas did not increase the leaching; rather it decreased compared with references. A possible explanation for this is a stimulation of the denitrification process in riparian zones as shown in other studies (Westling & Borg, 1998).

5 Conclusion

This study showed that treatment of both recharge and discharge areas resulted in quick and significant changes in stream water quality e.g. increased concentrations of Ca^{2+} , higher pH and ANC and a decreased concentration of inorganic aluminium. Treatment of recharge areas resulted in smaller but still significant effects on Ca^{2+} , pH and ANC in stream water but not on inorganic aluminium. The study shows that the effects of treated discharge areas

decrease with time, while it is indicated that the application on recharge areas gradually will improve the quality of the run off in the long term. So far the treatments were capable to reintroduce and maintain reproducing brown trout in the main stream.

In contrast to the repeated liming of surface waters, the positive effects were achieved by a single application six years ago. Liming of recharge areas restores the base saturation in the catchment, which has a long term potential to prevent acid run off without repeated treatments if the deposition of acidifying air pollutants continues to decrease. The long-term development of run off chemistry has to be monitored with continued measurements, but so far the total catchment treatment has shown to be a cost-effective method.

Acknowledgements This project started as an EU-Life financed project with the Regional Board of Forestry in South Götaland, the Swedish Environmental Protection Agency, the National Board of Forestry in Sweden and the County Administration Board of Halland as co-partners. The project was officially terminated in June 2001 but has been carried on by means from the National Board of Forestry and IVL Swedish Environmental Research Institute.

References

- Akselsson, C., Westling, O., & Örlander, G. (2004). Regional mapping of nitrogen leaching from clearcuts in southern Sweden. *Forest Ecology and Management*, 202, 235–243.
- Andersson, F., Hallbäcken, L., & Popovic, B. (1996). Liming and tree growth. In H. Staaf, T. Persson, & U. Bertills (Eds.), *Forest liming* (pp. 122–134). Stockholm, Sweden: The Swedish Environmental Protection Agency.
- Baurlaup, B. T., & Kleiven, E. (2004). Development of the brown trout (*Salmo trutta* L.) population after liming of Lake Store Hovvatn. In A. Hindar (Ed.), *Lake Store and Lille Hovvatn in Aust Agder County: a summary report after 25 years of research on acidification and liming* (pp. 95–112). Trondheim, Norway: Direktorat for Nature Management, Rep, 2004-1.
- Bell, R. (1992). Liming design and strategy at Loch Fleet. In G. Howells, & T. R. K. Dalziel (Eds.), *Restoring acid waters: Loch Fleet 1984–1990* (pp. 157–170). London: Elsevier.
- Borg, H., Ek, J., & Holm, K. (2001). Influence of acidification and liming on the distribution of trace elements in surface waters. *Water, Air and Soil Pollution*, 130, 1757–1762.
- Cirimo, C. P., & Driscoll, C. T. (1996). The impacts of a watershed CaCO_3 treatment in stream and wetland biogeochemistry in the Adirondack Mountains. *Biogeochemistry*, 31, 265–297.
- Clair, T. A., & Hindar, A. (2005). Liming for the mitigation of acid rain effects in freshwaters: A review of recent results. *Environmental Review*, 13, 91–128.

- Dickson, W., & Brodin, Y.-W. (1995). Strategies and methods for freshwater liming. In L. Henrikson, & Y.-W. Brodin (Eds.). *Liming of acidified surface waters* (pp. 24–81). Berlin, Heidelberg New York: Springer.
- Direktoratet för naturförvaltning (2001). Terrengekalkingsprojektet årsrapport 2000. Terrengekalking för å avgifte surt överflatevann. Notat 2001-4.
- Driscoll, C. T., Cirimo, C. P., Fahey, T. J., Blette, V. L., Baukavechas, P. A., Burns, D. A., et al. (1996). The experimental watershed liming study: comparison of lake and watershed neutralization strategies. *Biogeochemistry*, 32, 143–174.
- Falkengren-Grerup, U., Linnermark, N., & Tyler, G. (1987). Changes in acidity and cation pools of south Swedish soils between 1949 and 1985. *Chemosphere*, 16, 2239–2248.
- Fransman, B., & Nihlgård, B. (1995). Water chemistry in forested catchments after topsoil treatment with liming agents in South Sweden. *Water, Air and Soil Pollution*, 85, 895–900.
- Grieve, I. C. (1990). Effects of catchment liming and afforestation on the concentration and fractional composition of aluminium in the Loch Fleet catchments, SW Scotland. *Journal of Hydrology*, 11, 385–396.
- Gunn, J., Sein, R., Keller, B., & Beckett, P. (2001). Liming of acid and metal contaminated catchments for the improvement of drainage water quality. *Water, Air and Soil Pollution*, 130, 1439–1444.
- Hallbäck, L., & Zhang, L.-Q. (1998). Effects of experimental acidification, nitrogen addition and liming on ground vegetation in a mature stand of Norway spruce (*Picea abies* (L.) Karst) in SE Sweden. *Forest Ecology and Management*, 108, 201–213.
- Hindar, A., & Wright, R. F. (2005). Long-term records and modelling of acidification, recovery and liming at Lake Hovvatn, Norway. *Canadian Journal of Fisheries and Aquatic Sciences*, 62, 2620–2631.
- Hindar, A., Wright, R. F., Nilsen, P., Larssen, T., & Hogberget, R. (2003). Effects on stream water chemistry and forest vitality after whole-catchment application of dolomite to a forest ecosystem in southern Norway. *Forest Ecology and Management*, 180, 509–525.
- Huber, C. (1996). Einfluß der Kalkung auf den Stoffhaushalt eines stickstoffgesättigten Fichtenökosystems. Zusammenfassung wichtiger Ergebnisse aus den Kalkungsversuchen Högwald. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft*, 79, 141–144.
- Johansson, M.-B., Nilsson, T., & Olsson, M. (1999). *Miljökonsekvensbeskrivning av Skogsstyrelsens förslag till åtgärdsprogram för kalkning och vitalisering*. Jönköping, Sweden: The National Board of Forestry Publishing House, 168 pp.
- Larsson, P.-E., & Westling, O. (1997). Ytvatten i kalkade avrinningsområden. Årsrapport 1996. IVL Report B1279, 65 pp.
- Larsson, P.-E., Westling, O., & Abrahamsson, I. (2003). En integrerad strategi för kalk- och askspridning i avrinningsområden. IVL Report B1435, 33 pp.
- Larsson, P.-E., Uggla, E., & Westling, O. (2003). Långsiktiga effekter av skogsmarkskalkning på mark- och markvattenkemi. IVL Report B1524, 51 pp.
- Löfgren, S., & Westling, O. Modell för att beräkna kväveförluster från växande skog och hyggen i Sydsverige. Swedish University of Agricultural Sciences, Dept. of Environmental Assessment, Report 2002:1, Uppsala, Sweden (in Swedish).
- Lövblad, G., Henningsson, E., Sjöberg, K., Brorström-Lundén, E., Lindsog, A., & Munthe, J. (2004). Trends in Swedish background air 1980–2000. In J. Bartnicki, & G. Lövblad (Eds.). *EMEP Assessment Part II National Contributions* (pp. 211–220). Oslo, Norway: Norwegian Meteorological Institute.
- Olem, H. (1991). Liming acidic surface waters. Chelsea, MI: Lewis Publishers (331 pp).
- Olsson, M., Rosén, K., & Melkerud, P.-A. (1993). Regional modelling of base cation losses from Swedish forest soils due to whole-tree harvesting. *Applied Geochemistry* (Supplement No. 2), 189–194.
- Sverdrup, H., Martinson, L., Alveteg, M., Moldan, F., Kronnäs, V., & Munthe, J. (2005). Modeling recovery of Swedish Ecosystems from acidification. *Ambio*, 34, 25–31.
- The National Board of Forestry (2005). *Swedish Statistics Yearbook of Forestry 2005*. Jönköping, Sweden: The National Board of Forestry Publishing House, 332 pp.
- Traaen, T. S., Frogner, T., Hindar, A., Kleiven, E., Lande, A., & Wright, R. F. (1997). Whole catchment liming at Tjønnsstrond, Norway: an 11-year record. *Water, Air and Soil Pollution*, 94, 163–180.
- Westling, O., & Borg, G. (1998). Gödsling av skogsmark med fosfor och kalium – effekter på mark- och ytvatten. In H.-Ö. Nohrstedt (Ed.), *Effects of nitrogen-free forest fertilization on soil and water* (pp. 81–119). Stockholm, Sweden: The Swedish Environmental Protection Agency.
- Westling, O., & Hultberg, H. (1990). Liming and fertilization of acid forest soil: Short-term effects on run off from small catchments. *Water, Air and Soil Pollution*, 54, 391–407.
- Wickström, H., Eriksson, H., Berggren, H., Westling, O., Larsson, P.-E., Abrahamsson, I., et al. (2004). Projekt Nissadalen – En integrerad strategi för kalkning och askspridning i hela avrinningsområden. Report 4:2003. Jönköping, Sweden: The National Board of Forestry Publishing House, 199 pp.
- Wilander, A., & Lundin, L. (2000). Recovery of surface waters and forest soils in Sweden. In P. Warfvinge, & U. Bertills (Eds.), *Recovery from Acidification in the natural environment: Present knowledge and future scenarios* (pp. 53–66). Trelleborg, Sweden: The Swedish Environmental Protection Agency, Report 5034.

Cost-effectiveness Analysis of Reducing the Emission of Nitrogen Oxides in Asia

Ken Yamashita · Fumiko Ito · Keigo Kameda ·
Tracey Holloway · Matthew P. Johnston

Received: 16 June 2005 / Accepted: 6 June 2006 / Published online: 25 January 2007
© Springer Science + Business Media B.V. 2007

Abstract The purpose of this study is to evaluate cost-effective reduction strategies for nitrogen oxides (NO_x) in the Asian region. The source-receptor relationships of the Lagrangian “puff” model of long-range transportation, ATMOS-N, were used to calculate the wet/dry deposition of the nitrogen (N) in Asia. Critical loads of N deposition in Asia were calculated from the relationships between the critical load of sulfur (S) and balance of N in and out using the data of S critical load of RAINS-ASIA. The cost

functions of N reduction of Asian countries were derived by the regression analysis with the data of cost functions of European countries used in RAINS. In order to assess the environmental impact, the gaps between N deposition and critical load of N were calculated. The emission of NO_x was reduced in some cases of this model, and the changes of gaps between N deposition and critical load were observed as well as the changes of the reduction cost. It is shown that a uniform reduction of NO_x emissions by countries in Asia is not cost-effective strategy.

K. Yamashita (✉)
Niigata Prefectural Government,
4-1 Shinko-cho, Niigata City 950-8570, Japan
e-mail: MHD04003@nifty.ne.jp

F. Ito
Tokyo Metropolitan University, 1-1 Minamiosawa,
Hachioji City, Tokyo 192-0397, Japan
e-mail: itofumi@center.tmu.ac.jp

K. Kameda
School of Policy Studies, Kwansei Gakuin University,
2-1 Gakuen, Mita City, Hyogo 669-1337, Japan
e-mail: kameda@ksc.kwansei.ac.jp

T. Holloway · M. P. Johnston
Center for Sustainability and the Global Environment
(SAGE), University of Wisconsin – Madison,
1710 University Ave., Madison, WI 53726, USA

T. Holloway
e-mail: taholloway@wisc.edu

M. P. Johnston
e-mail: mjohnston@wisc.edu

Keywords acid deposition · Asia · cost function ·
critical load · integrated assessment model ·
nitrogen oxides · RAINS-ASIA

1 Introduction

Recently increasing emissions of sulfur dioxides (SO_2) and nitrogen oxides (NO_x) due to great economic growth in Asia are a major concern for serious damage to ecosystems caused by acid deposition. In the 1990s in Europe, the integrated assessment model, the Regional Air pollution INformation and Simulation (RAINS) model, was developed to provide the scientific basis to reduce cost-effectively the emission of SO_2 as a precursor of acid deposition (Alcamo, Shaw, & Hordijk, 1990; Cofala et al., 2003; Cofala & Syri, 1998b). RAINS was the useful tool in the process of concluding protocol of Convention on Long-Range Transboundary Air Pollution (CLRTAP). Considering

overall ecosystem effects by nitric acid deposition, eutrophication and ground-level ozone, RAINS has subsequently become an important tool for protocols of CLRTAP to reduce the emission of NO_x , ammonia (NH_3) and volatile organic compounds (VOCs) (Amann, Cofala, Heyes, Klimont, & Schopp, 1999).

In Asia the assessment model for acid deposition, RAINS-ASIA, was developed in the late 1990s for cost-effective control of SO_2 emissions in this region (Downing, Ramankutty, & Shah, 1997). To date, however, official versions of RAINS-ASIA do not contain NO_x , NH_3 or VOCs. Here we create a new module for calculating the reduction cost of the NO_x emissions and examine the options for reduction utilizing the methodology of RAINS and RAINS-ASIA.

2 Acid Deposition Problems and Regional Cooperation in Europe, North America and Asia

Acidification throughout Europe and North America has been an important research focus for environmental scientists since the 1960s. The Cooperative Programme for the Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) was initiated in 1977 and led to the 1979 signing of CLRTAP by the most countries of Eastern and Western Europe, the United States and Canada.

In North America, it was warned in the early 1970s that the acidification damage to lakes, streams and forests was observed in the northeastern US and Canada (Howard & Perley, 1980). Canada and the US established the Canadian Network for Sampling Precipitation (CANSAP) in 1976 and the National Atmospheric Deposition Program (NADP) in 1978, respectively (Carmichael, Peters, & Saylor, 1990; EPA, 2000).

The Acid Deposition Monitoring Network in East Asia (EANET¹) started its activities in 1998 considering the rapid economic growth and consequent increasing emission of air pollutants in the East Asian region (EANET, 2000). EANET, which includes 12 countries as of June 2005, has been carrying out cooperative activities such as reliable monitoring of wet and dry deposition and effects on ecosystems as the first step to assess the acid deposition problems in East Asia. In South Asia, the regional cooperative

program on air pollution, the Malé Declaration,² was initiated in 1998 and has commenced its activities.

3 The Integrated Assessment Models: Reduction of Emission and Its Cost

Integrated assessment models may be employed to help understand complicated acid deposition problems. An atmospheric model simulates the long-range transportation, chemical transformation and the amount of deposition of air pollutants, and an economic model provides the vision of the cause and the reduction cost of emission of SO_2 , NO_x , NH_3 and VOCs. This type of multi-disciplinary model aids scientists and policy makers in considering different abatement options. The RAINS integrated assessment framework includes five components; (a) emission inventory, (b) atmospheric transport and transformation, (c) environmental effects, (d) abatement and mitigation options, and (e) monetary evaluation (Amann, 2001; Amann et al., 1999; Hordijk & Kroeze, 1997).

4 Development of the Model of Reducing NO_x Emission and Estimation of its Cost in Asia

Our study follows the RAINS methodology to assess N controls in Asia. We follow five steps in the evaluation process: (a) calculation of N deposition from the emission inventory of NO_x using the transportation/deposition model, (b) derivation of critical load of N from the critical load value used in RAINS-ASIA, (c) estimation of the national cost function of the NO_x emission, (d) evaluation of change of adverse effects on ecosystem using critical load of N in some cases of NO_x emission reduction, (e) case simulation of reduction cost of each country of NO_x emission control (Amann & Klaasen, 1995).

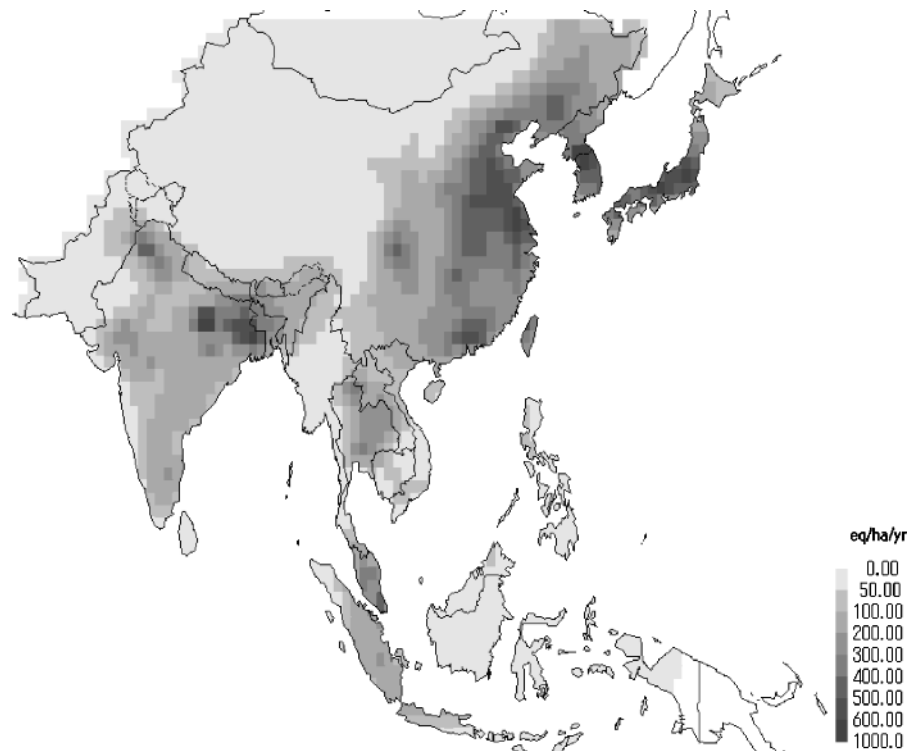
4.1 Emission Inventory

The NO_x emission inventory of the University of Iowa's Center for Global and Regional Environmental Research (CGRER)³ was used in this study since it was the most recent estimate (Aardenne van, Carmichael,

¹ <http://www.eanet.cc/>

² <http://www.rrcap.unep.org/issues/air/Maledec/>

³ http://atmos.cgrer.uiowa.edu/EMISSION_DATA/index_16.htm#

Fig. 1 Deposition of N

Levy, Streets, & Hordijk, 1999; Klimont, 2001; Yienger & Levy, 1995), developed in support of the Aerosol Characterization Experiments (ACE)-Asia and Transport and Chemical Evolution over the Pacific (TRACE-P) experiments (Woo et al., 2002). The domain covers 13°S~53°N latitude and 60°E~157°E longitude, and the resolution is 1°×1°, including 22 Asian countries and 60 sub-regions for the year 2000. The total amount of NO_x emission in Asia was estimated 26.77 Tg-NO₂/year.

4.2 Model of Transportation and Deposition

This study estimated N deposition through the use of annual source-receptor relationships (SRRs) calculated with the regional transport and chemistry model, ATMOS-N⁴ (Holloway, Levy, & Carmichael, 2002). Although the original SRRs calculations used other emission inventories, these values were scaled to the CGRER estimate, assuming a linear relationship between emissions and deposition. As illustrated in Fig. 1, deposition is highest in the eastern part of China,

the eastern part of India, the northern part of R. of Korea and the middle part of Japan. ATMOS-N is a Lagrangian “puff” model in which emissions are modeled as non-interacting puffs advected horizontally and split in three vertical layers. Data of winds and precipitation used in ATMOS-N are National Centers for Environmental Prediction (NCEP) reanalysis data in 1990.

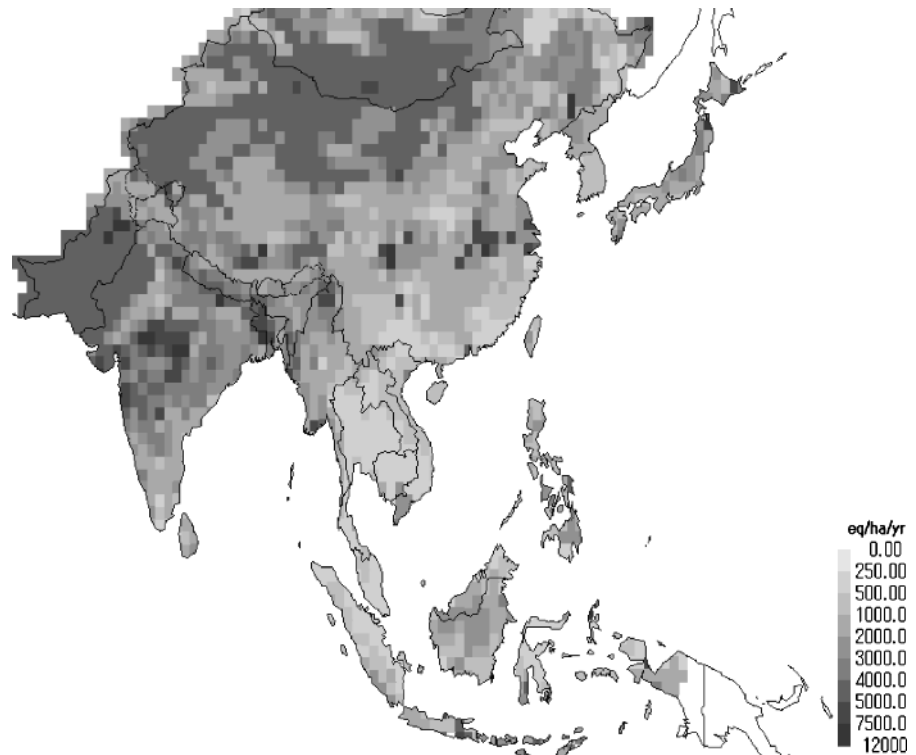
4.3 Critical Load of N

Critical loads are the threshold value of the amount of acid deposition above which adverse effects can be observed on ecosystems, and below which ecosystems are protected. Critical load levels are derived from site-specific topography, soil and ecosystem of the area. Although no such precise level exists in nature, critical loads have been a useful method for assessing protection levels for environmental decision-making (Posch, de Smet, Hettelingh, & Downing, 2001).

Critical loads of S in Asia were calculated (Hettelingh, Sverdrup, & Zhao, 1995) with Steady-State Mass Balance (SSMB) methodology and used in RAINS-ASIA (Shindo & Hettelingh, 2000), but critical loads of N in whole Asian region have not yet been calculated. Critical loads of N were

⁴ ATMOS-N was the only model that published annual SRRs of NO_x in Asia as of 2004.

Fig. 2 Critical load of N ($CL_{\max}(N)-25\%$)



calculated in this study using the relationships between critical loads of S^5 and N. In order to avoid the uncertainty of SSMB, 25-percentile critical load (protecting 75% of the ecosystems) were used instead of using the lower percentile such as 5-percentile critical load.

The critical loads of N are expressed by means of mass balances for S and N as following equations (Posch, De Vries, & Hettelingh, 1995):

$$CL_{\max}(N) = CL_{\min}(N) + CL_{\max}(S)/(1 - f_{de}) \quad (1)$$

$$CL_{\min}(N) = Nu + Ni \quad (2)$$

$$CL_{nut}(N) = Nu + Ni + N_{le(crit)}/(1 - f_{de}) \quad (3)$$

Where $CL_{\max}(S)$ is the maximum critical load for sulfate, $CL_{\max}(N)$ is the maximum critical load for nitrate, $CL_{\min}(N)$ is the minimum critical load for nitrate, $CL_{nut}(N)$ is the critical load for nutrient nitrate, f_{de} is the denitrification fraction, Nu is the net growth uptake, Ni is the long-term immobilization, and $N_{le(crit)}$ is the critical leaching of nitrate.

⁵ The critical load values calculated in RAINS-ASIA phase II were used here.

In this study Nu is assumed zero because uptake and release of nutrients can be considered to be balanced in a natural forest with stable amount of plants. The constant value of f_{de} corresponds to a soil type is adopted in many studies in Europe (e.g. Posch, Hettelingh, Slootweg, & Downing, 2003; Posch et al., 1995). Regarding value of f_{de} , 0.1 was applied to all grid cells here as a simple estimation. Though there are few studies on f_{de} in Asia, a study used 0.1 or 0.5 as the value of f_{de} corresponding to wet of a soil type of

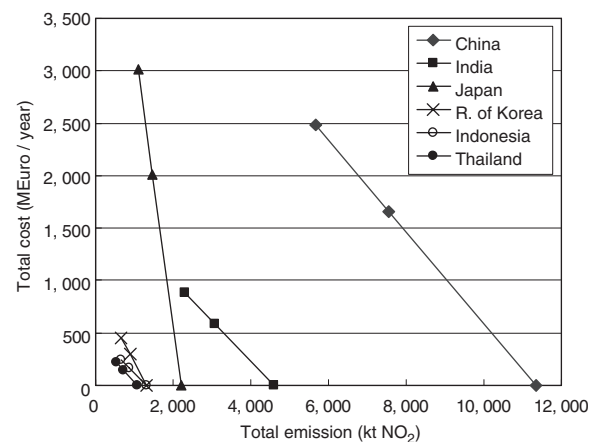


Fig. 3 Estimated cost curves of group III

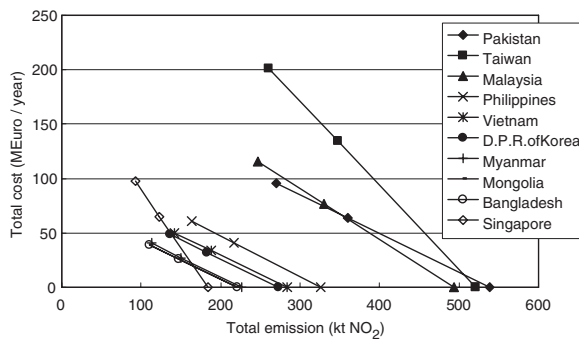


Fig. 4 Estimated cost curves of group II

Japan (Hayashi & Ozaki, 2001). The value of 0.1 will avoid underestimation of adverse effects on ecosystems. The critical load of N for eutrophication ($CL_{nut}(N)$) is not used. Only the aspect of acidification of N is considered in this study since the information on critical leaching of N is not sufficient in Asia. Figure 2 shows $CL_{max}(N)$ of 25-percentile.

4.4 Estimation of the Cost Function

In this section the cost functions of reducing anthropogenic NO_x emission of countries in Asia are estimated from those in Europe used in RAINS.

4.4.1 Regression Analysis for Cost Function of NO_x Emission Control of RAINS

In RAINS model the cost function of the reduction of NO_x emission were created for each country and year (Cofala & Syri, 1998a). It is assumed that the most cost-effective option of NO_x reduction is preferentially used, so controls are implemented in order of descending cost-effectiveness. Control options are applied to both stationary and mobile sources, with cost functions⁶ of 27 countries in Europe for 2000 used to derive the cost functions of 22 countries in Asia.

For the regression analysis, it was assumed that the total cost of NO_x emission reduction was the function of the NO_x emission, Gross Domestic Product (GDP) and GDP per capita (GDP/C). The reasons of the assumption were following points;

- (a) The total cost of NO_x reduction was proportional to the amount of NO_x emission reduction,

⁶ The data was downloaded from the web site of IIASA (<http://www.iiasa.ac.at/web-apps/tap/RainsWeb/>) in September 2004.

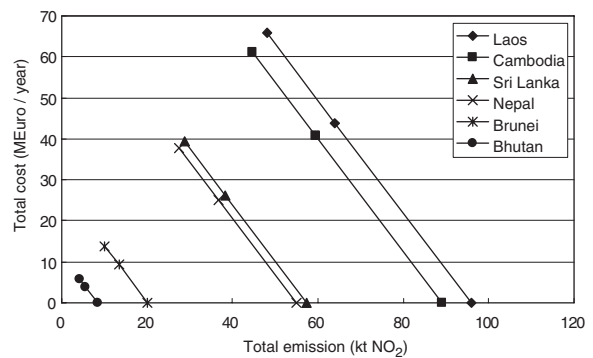


Fig. 5 Estimated cost curves of group I

- (b) GDP was relative to the total amount of NO_x emission, and
- (c) GDP/C was related to the shape of cost function as the proxy variable, which showed the level of technology of the country.

As a result of multiple regression analysis, logarithmic equations had R^2 value less than 0.4 (R^2 is the coefficient of multiple determination), and quadratic equations had the problem of the inconsistent shape of curve with the original curves though some equations had R^2 more than 0.9. Consequently the regression line (4) was the more appropriate estimated function ($R^2 > 0.8$).

$$\begin{aligned} \text{Total cost} = & \alpha + \beta \text{ GDP} + \gamma \text{ emission} \\ & + \delta \text{ GDP/C} + \zeta \text{ emission GDP} \\ & + \eta \text{ emission GDP/C} + \varepsilon \end{aligned} \quad (4)$$

Where the α , β , γ , δ , ζ and η are coefficients, and ε is disturbance term.

The total cost functions of European countries in RAINS were categorized by their shapes of curve into three types (A, B, and C). The cost curve of type A⁷ is concave upward, the cost curve of type B⁸ is linear, and the cost curve of type C⁹ is other shape. The type C was, therefore, considered to be excluded from the

⁷ England, Italy, Poland, Netherlands, Belgium, Greece, Portugal, Czech, Norway, Finland, Denmark, Austria, Hungary, Ireland, Slovakia.

⁸ Germany, France, Spain, Sweden, Switzerland, Slovenia, Lithuania, Estonia, Luxembourg, Cyprus, Malta.

⁹ Latvia.

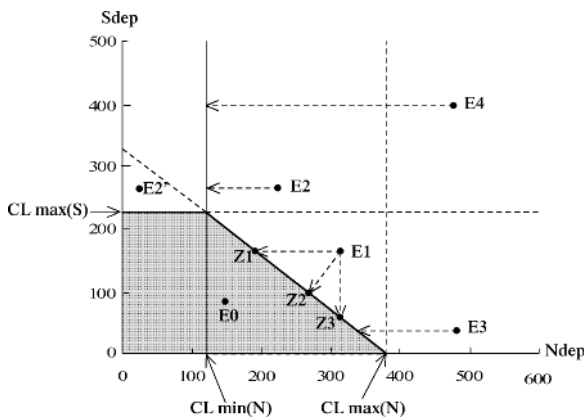


Fig. 6 Relationship between N and S deposition and the critical load of sulfur and nitrogen (Source: Posch et al., 1995, modified by Yamashita)

analysis as the outlier. The estimated regression equations by the multiple regression analysis are as follows (figures in parentheses are *t*-values);

Type A:

$$\begin{aligned} \text{Total cost} = & 56.58 + 0.001935 \times \text{GDP} - 0.3395 \\ & \times \text{emission} - 6.654 \times 10^{-8} \\ & \times (\text{emission} \cdot \text{GDP}) - 3.140 \times 10^{-5} \\ & \times (\text{emission} \cdot \text{GDP}/C) \end{aligned} \quad (5)$$

Type B:

$$\begin{aligned} \text{Total cost} = & 107.6 + 0.003327 \times \text{GDP} - 1.370 \\ & \times \text{emission} - 2.893 \times 10^{-7} \\ & \times (\text{emission} \cdot \text{GDP}) - 0.009412 \\ & \times \text{GDP}/C \end{aligned} \quad (6)$$

It is noted with the obtained regression lines that the cost is over-estimated for the point of no-reduction (full emission) to half-reduction (half of emission) of the total emission, and under-estimation for over half-reduction of the total emission since the gap between obtained cost line and the cost curve of RAINS is growing when the reduction goes over the half of emission.

It is assumed by the relation between the NO_x emission and the type of cost function that the coun-

tries are categorized into three groups by the cost functions of RAINS: group (I) contained cost functions of type B with the NO_x emission under 100 kt- NO_2 /year, group (II) contained cost functions of type A with the NO_x emission between 100 to 1,000 kt- NO_2 /year, group (III) contained cost functions of A and B with the NO_x emission over 1,000 kt- NO_2 /year.

4.4.2 Estimation of Cost Function of NO_x Emission Control in Asia

The estimated cost functions of type A and type B (Eqs. 5 and 6) were used to derive the cost functions of countries in Asia since the equations are thought to be available also for Asian countries in spite of differences of economic condition between Europe and Asia. The cost functions of 22 Asian countries were estimated sorting the countries by NO_x emission based on the same criteria that were employed in defining cost curves for European countries. Among countries of group III only Japan was categorized as type B since Japan has many options to reduce the emission of NO_x from the stationary and mobile sources, similar to Germany. The estimated cost curves of the group III,¹⁰ the group II¹¹ and the group I¹² are shown in Figs. 3, 4 and 5, respectively. The constant terms are adjusted so that the total cost equals zero at the point of no-reduction in Figs. 3, 4 and 5.

4.5 Reduction Cost of NO_x Emission

4.5.1 Deposition and Critical Load of S and N

The relationship between deposition of S and N exceeding the critical load (Ex) is expressed as follows;

$$\text{Ex}(S + N) = S_{\text{dep}} + N_{\text{dep}} - \text{CL}(S + N) \quad (7)$$

Where $\text{Ex}(S+N)$ is the deposition of S and N exceeding the critical load, S_{dep} and N_{dep} are deposition of S and N respectively, and $\text{CL}(S+N)$ is the critical load of S and N (Posch et al., 1995). The Fig. 6 shows its relationship.

¹⁰ China, India, Japan, R. of Korea, Indonesia, Thailand.

¹¹ Pakistan, Taiwan, Malaysia, Philippines, Vietnam, D.P.R. of Korea, Myanmar, Mongolia, Bangladesh, Singapore.

¹² Lao, Cambodia, Sri Lanka, Nepal, Brunei, Bhutan.

Fig. 7 The cells of $Ex(S+N) \geq 0$ in the area of $S_{dep} \leq CL_{max}(S)$



Fig. 8 The cells of $Ex(S + N \times 2/3) \geq 0$ in the area of $S_{dep} \leq CL_{max}(S)$



Fig. 9 The cells of $Ex(S+N/2) \geq 0$ in the area of $S_{dep} \leq CL_{max}(S)$



Fig. 10 The cells of $N_{dep} - CL_{min}(N)$ with no reduction of NO_x emission

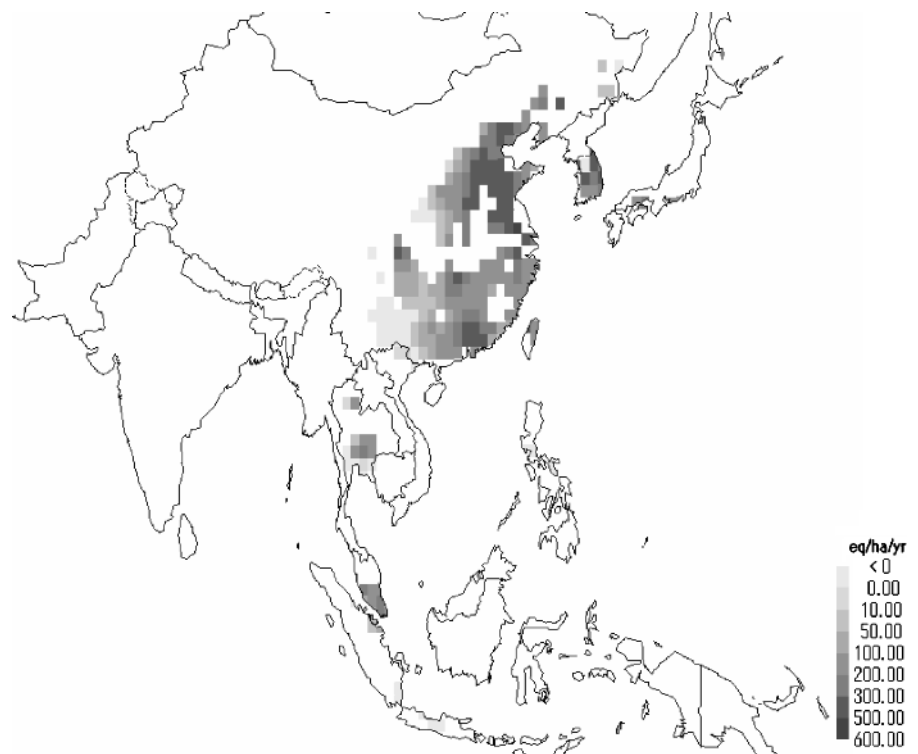


Fig. 11 The cells of $N_{\text{dep}} - CL_{\text{min}}(N)$ with 33% reduction of NO_x emission

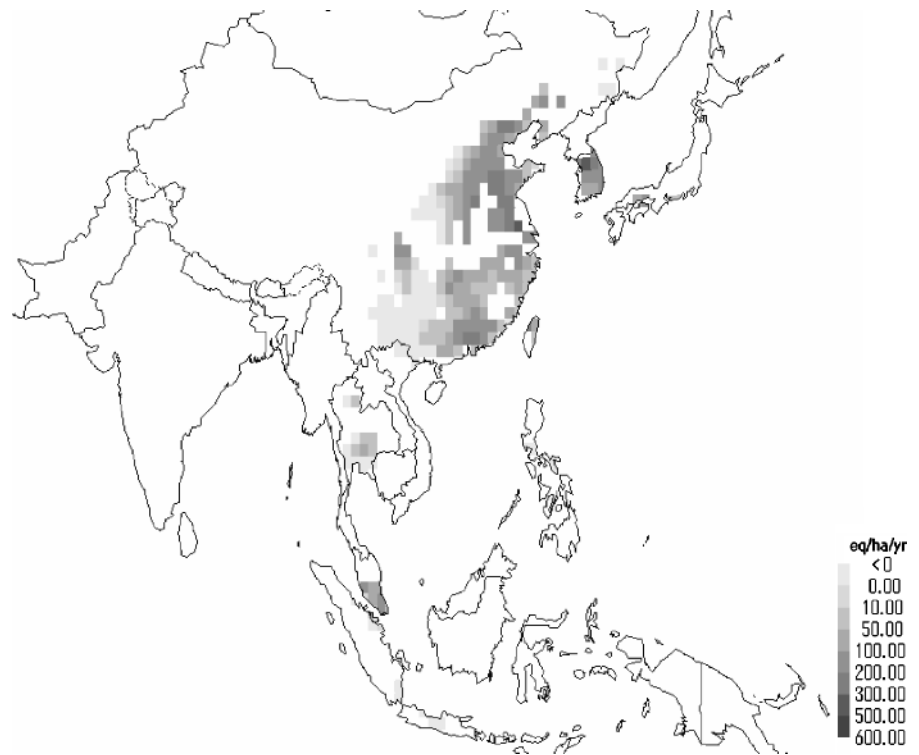


Fig. 12 The cells of $N_{\text{dep}} - CL_{\text{min}}(N)$ with 50% reduction of NO_x emission

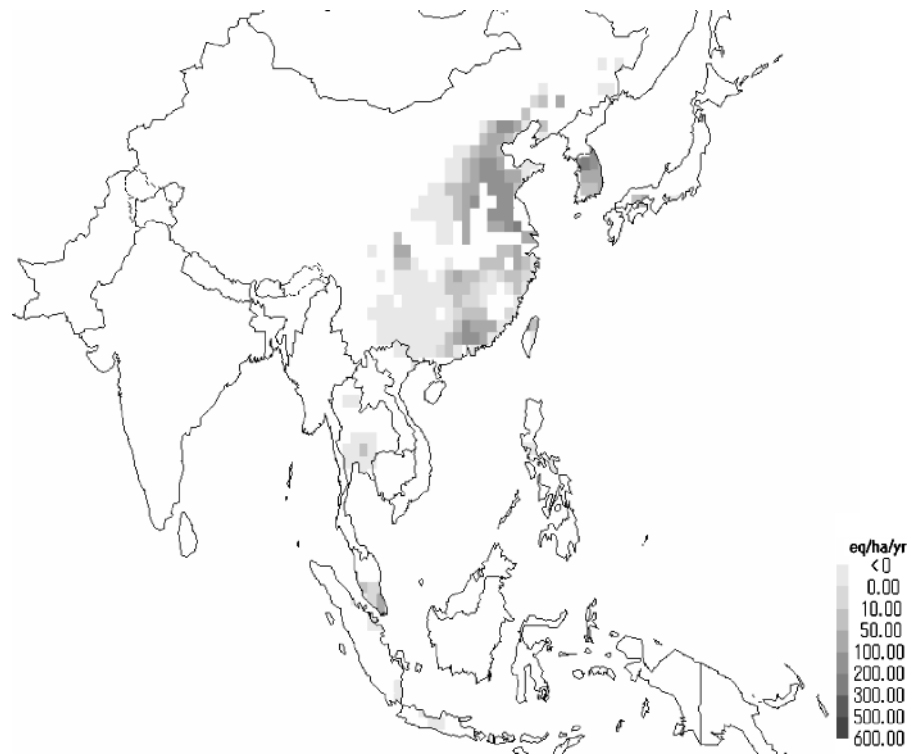


Table 1 Reduction of NO_x emission and the total cost of each countries in Asia

Country	Group of countries	Type of cost function	G D P (MUS\$)	GDP per capita (MUS\$)	NO _x emission in 2000 (kt NO ₂)	Total cost of reduction of NO _x emission at 33% (MEuro/year)	Total cost of reduction of NO _x emission at 50% (MEuro/year)
China	III	A	1,079,386.4	846.4	11,346.8	1,656.4	2,484.6
India	III	A	468,225.7	460.4	4,590.9	589.4	884.1
Japan	III	B	4,744,660.0	37,408.0	2,198.1	2,009.7	3,014.6
R. of Korea	III	A	461,518.5	9,853.1	1,322.0	299.5	449.2
Indonesia	III	A	152,226.1	719.5	1,317.4	163.5	245.2
Thailand	III	A	122,569.3	2,012.0	1,086.0	148.7	223.1
Pakistan	II	A	58,663.9	411.2	539.3	64.1	96.1
Taiwan	II	A	292,900.9	13,184.2	520.7	134.2	201.2
Malaysia	II	A	90,161.1	3,920.0	494.0	77.2	115.8
Philippines	II	A	74,862.0	988.8	326.2	40.8	61.2
Vietnam	II	A	31,349.0	401.0	283.0	33.4	50.1
D.P.R. of Korea	II	A	10,608.0	476.0	273.3	32.4	48.5
Myanmar	II	A	32,988.0	694.0	226.0	27.4	41.1
Mongolia	II	A	970.0	388.0	220.7	25.9	38.8
Bangladesh	II	A	45,470.1	329.6	220.3	25.9	38.9
Singapore	II	A	91,473.3	22,754.6	184.6	65.2	97.8
Rao	I	B	1,733.0	328.0	96.0	43.9	65.8
Cambodia	I	B	3,367.0	256.0	89.1	40.7	61.1
Sri Lanka	I	B	16,331.8	878.5	57.4	26.3	39.5
Nepal	I	B	5,338.3	227.0	55.1	25.2	37.8
Brunei	I	B	4,316.0	12,922.0	20.2	9.2	13.9
Bhutan	I	B	483.0	234.0	8.4	3.9	5.8
Total			7,789,601.4	109,692.5	25,475.5	5,542.7	8,314.1

There is no adverse effect on ecosystems if the combination of S and N of critical load is within the shaded domain ($E_x \leq 0$) in Fig. 6. Two cases are explained to move the points E1, E2, E3 and E4 into the shaded area.

(a) $S_{\text{dep}} \leq CL_{\text{max}}(S)$:

In this case the points E1 and E3 are to be moved onto the isoline of critical load function (boundary line of shaded area). Considering the reduction of N_{dep} in this study, the route on E1 to Z1 is considered although there are other possible routes to the isoline (E1 to Z2 or Z3). The different paths to the isoline mean the different costs. E3 is the point which the N_{dep} should be reduced because N_{dep} of E3 exceeds $CL_{\text{max}}(N)$.

(b) $S_{\text{dep}} > CL_{\text{max}}(S)$:

In this case the point E2 should reduce S_{dep} since the S_{dep} exceeds $CL_{\text{max}}(S)$. This study only considers

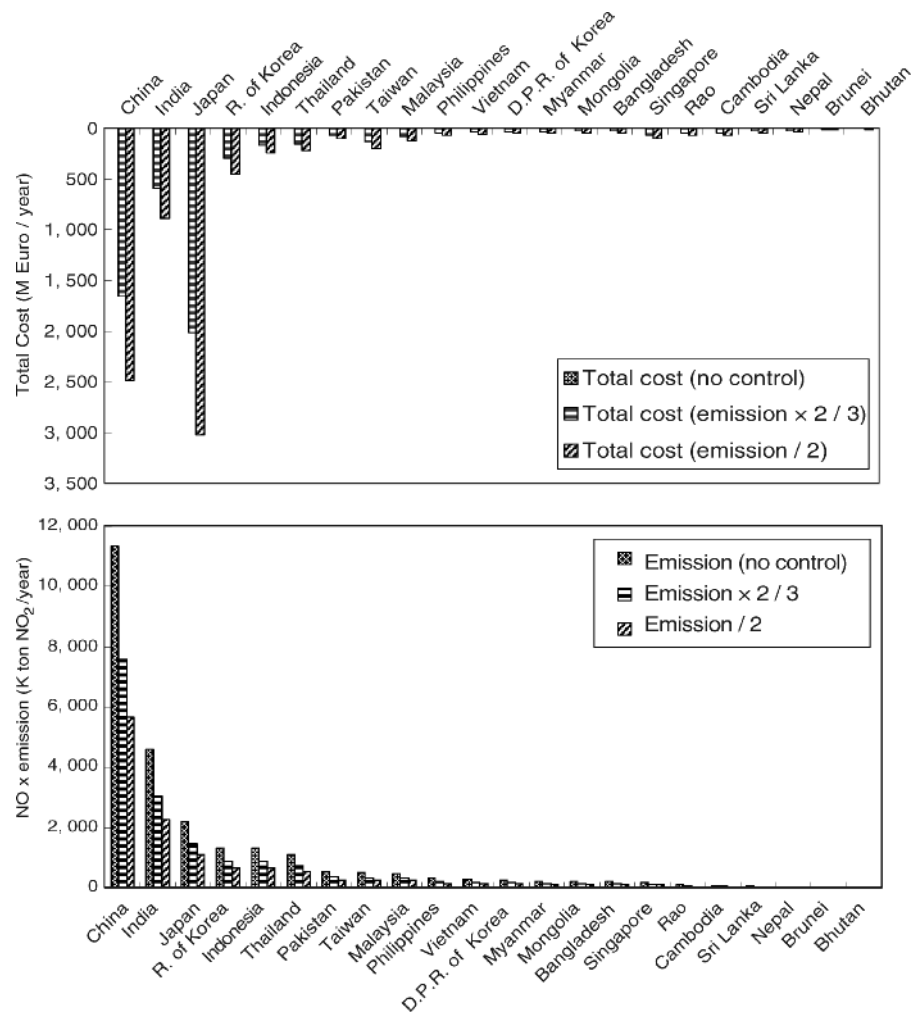
the reduction of N_{dep} , therefore, the points E2 and E4 are to be moved to the $CL_{\text{min}}(N)$.

4.5.2 Reduction of NO_x Emission and Consequent Change of Gap between Critical Load and N Deposition

The impact of NO_x emission reductions in a source grid cell is calculated with the SRRs, relative to the initial (no control) level of N deposition in each receptor cell. In order to shorten the calculation time three cases are examined here: no control, a half emission reduction, and one third emission reduction, relative to both ‘baseline’ and ‘current legislation’ emission scenarios. Two cases of sulfur deposition to critical load are examined in the following (a) and (b).

(a) $S_{\text{dep}} \leq CL_{\text{max}}(S)$:

Fig. 13 Reduction of NO_x emission and total cost



Ex with the reduction of NO_x emission at 0, 33 and 50% are shown in Figs. 7, 8 and 9,¹³ respectively. The shaded grid cells have the deposition exceeded critical load, the blank grid cells mean the area of $S_{\text{dep}} > \text{CL}_{\text{max}}(\text{S})$, and the area ($\text{Ex} < 0$) is also shown in the figures (the most lightly shaded).

(b) $S_{\text{dep}} > \text{CL}_{\text{max}}(\text{S})$:

The results of $N_{\text{dep}} - \text{CL}_{\text{min}}(\text{N})$ with the reduction of NO_x emission in the proportion of 0, 33 and 50% are shown in Figs. 10, 11 and 12. The blank grids mean the area of $S_{\text{dep}} \leq \text{CL}_{\text{max}}(\text{S})$, and the area

($N_{\text{dep}} - \text{CL}_{\text{min}}(\text{N}) < 0$) is also shown in the figures (the most lightly shaded).

4.5.3 Reduction of NO_x Emission and its Cost

Using the national cost functions estimated in 4.4.2, the two cases of total cost of NO_x emission reduction were calculated. The uniform reduction of NO_x emission is not cost-effective as illustrated by Table 1 and Fig. 13. For instance in the case of reduction at 33%, though the amount of reduction of NO_x emission of Japan is one-fifth (732 kt/year) as much as that of China, the cost of Japan is 1.2 times (3,014 MEuro/year) as much as that of China. The NO_x emission of top six countries (China, India, Japan, R. of Korea, Indonesia and Thailand) is 85.8%

¹³ Mapping program of RAINS-ASIA is used to show the result of calculation.

of the total NO_x emission in Asia. Optimization to minimize the cost of reduction of NO_x and SO_2 can be calculated with our model, although we have not yet performed an optimization analysis.

5 Conclusions

In this study, we have developed a method for estimating the cost of reduction of the emission of NO_x in Asia.

It is expected that this study can provide the useful information for cost-effective control of acid deposition problems in Asia. For instance, how much should NO_x emissions be reduced in developing countries (China and India) that emit much of NO_x versus a developed country (Japan) in terms of equity?

In light of the wide range of economic conditions in Asia, the appropriate policy options must be explored very carefully. In this connection, EANET, the only cooperative international initiative for the acid deposition problems in East Asia, is expected to play the important role (Otoshi et al., 2001; Sato & Yamashita, 2004; Yamashita & Sato, 2005).

This study should be considered preliminary, with room for further investigation including: (a) derivation of the critical load of N from soil and vegetation data from the viewpoint of eutrophication, (b) examination of the cost curve with the shape of steep increasing rate, (c) using the emission inventory and deposition including N of ammonia, (d) cumulative estimation of the cost function from the emission inventory in the future. Furthermore, the optimization calculation to minimize the reduction cost of S and N simultaneously is necessary for integrated cost-effective analysis of adverse effects on ecosystem by acid substances. Ozone problems related to acid deposition should also be taken into account from the viewpoint of cost-effectiveness as well as multi-effect and multi-pollutant approach.

Acknowledgement The authors would like to thank Kentaro Hayashi, Kazuhide Matsuda, Hiroyuki Sase and anonymous reviewers for helpful comments in revising this paper, RAINS-ASIA Phase II for support.

References

Aardenne van, J. A., Carmichael, G. R., Levy II, H., Streets, D., & Hordijk, L. (1999). Anthropological NO_x emissions in

- Asia in the period 1990–2020. *Atmospheric Environment*, 33, 633–646.
- Alcamo, J., Shaw, R., & Hordijk, L. (1990). *The RAINS model of acidification: Science and strategies in Europe*. Dordrecht/Boston/London: Kluwer.
- Amann, M. (2001). Emission inventories, emission control options and control strategies: An overview of recent developments. *Water, Air, and Soil Pollution*, 130, 43–50.
- Amann, M., Cofala, J., Heyes, C., Klimont, Z., & Schopp, W. (1999). The RAINS model: A tool for assessing regional emission control strategies in Europe. *Pollution Atmospherique-December*, 1999, pp. 41–63.
- Amann, M., & Klaassen, G. (1995). Cost-effective strategies for reducing nitrogen deposition in Europe. *Journal of Environmental Management* (1995), 43, 289–311.
- Carmichael, G. R., Peters, L. K., & Saylor, R. D. (1990). The STEM-II regional scale acid deposition and photochemical oxidant model-I. An overview of model development and applications. *Atmospheric Environment*, 25A(10), 2077–2090.
- Cofala, J., Amann, M., Gyarmas, F., Schoepp, W., Boudri, J. C., Hordijk, L., et al. (2003). Cost-effective control of SO_2 emissions in Asia. *Journal of Environmental Management*, 72, 149–161.
- Cofala, J., & Syri, S. (1998a). Nitrogen oxides emissions, abatement technologies and related costs for Europe in the RAINS model database, Interim Report IR-98-88, IIASA, Laxenburg, Austria.
- Cofala, J., & Syri, S. (1998b). Sulfur emissions, abatement technologies and related costs for Europe in the RAINS model database, Interim Report IR-98-035, IIASA, Laxenburg, Austria.
- Downing, R. J., Ramankutty, R., & Shah, J. J. (1997). RAINS-ASIA: An assessment model for acid deposition in Asia. The World Bank, Washington (pp. 1–67).
- EANET (2000). Report on the Acid Deposition Monitoring of EANET during the Preparatory Phase – Its Results, major Constraints and Ways to Overcome Them-. Interim Scientific Advisory Group of the EANET, 2000.
- Environmental Protection Agency (EPA) (2000). Analysis of the Acid Rain Deposition and Ozone Control Act (S.172), Prepared for: The Senate Subcommittee on Clean Air, Wetlands, Private Property, and Nuclear Safety. U.S.EPA, Office of Air and Radiation, Clean Air Markets Division.
- Hayashi, K., & Ozaki, M. (2001). Acid deposition and critical load of Tokyo. *Water, Air and Soil Pollution*, 130, 1211–1216.
- Hettelingh, J.-P., Sverdrup, H., & Zhao, D. (1995). Deriving critical loads for Asia. *Water, Air and Soil Pollution*, 85, 2565–2570.
- Holloway, T., Levy II, H., & Carmichael, G. (2002). Transfer of reactive nitrogen in Asia: Development and evaluation of a source-receptor model. *Atmospheric Environment*, 36, 4251–4264.
- Hordijk, L., & Kroeze, C. (1997). Integrated assessment models for acid rain. *European Journal of Operational Research*, 102(1997), 405–417.
- Howard, R., & Perley, M. (1980). Acid rain – The North American forecast. Toronto, Canada: House of Anansi Press.
- Klimont, Z. (2001). Projections of SO_2 , NO_x , NH_3 and VOC emissions in east Asia up to 2030. *Water, Air, and Soil Pollution*, 130, 193–198.

- Otoshi, T., Fukuzaki, N., Li, H., Hoshino, H., Sase, H., & Suzuki, K. (2001). Quality control and its constraints during the preparatory-phase activities of the acid deposition monitoring network in East Asia (EANET). *Water, Air, and Soil Pollution*, 130, 1613–1618.
- Posch, M., Hettelingh, J.-P., Slootweg, J., & Downing, R. J. (Eds.) (2003). *Modelling and mapping of critical thresholds in Europe, CCE Status Report 2003*. ICP M&M Bilthoven, Netherlands: Coordination Center for Effects, National Institute for Public Health and the Environment (RIVM).
- Posch, M., de Smet, P. A. M., Hettelingh, J.-P., & Downing, R. J. (Eds.) (2001). *Calculation and mapping of critical thresholds in Europe, Status Report 2001*. Bilthoven, Netherlands: Coordination Center for Effects, National Institute for Public Health and the Environment (RIVM).
- Posch, M., De Vries, W., & Hettelingh, J.-P. (1995). Critical loads of sulfur and nitrogen. In M. Posch, P. A. M. De Smet, J.-P. Hettelingh, R. J. Downing (Eds.), *Calculation and mapping of critical loads in Europe, Status Report 1995* (pp. 31–41). Bilthoven, Netherlands: Coordination Center for Effects (RIVM).
- Sato, J., & Yamashita, K. (2004). Present status and constraints of the acid deposition monitoring network in East Asia (EANET). *Journal of Koeki Studies*, 4(1), 50–56, (in Japanese).
- Shindo, J., & Hettelingh, J.-P. (Eds.) (2000). IMPACT Module, RAINS-ASIA Phase II Workshop, Tsukuba, 2000.
- Woo, J. H., Streets, D. G., Carmichael, G. R., Dorwart, J., Thongboonchoo, N., Guttikunda, S., et al. (2002). Development of the emission inventory system for supporting TRACE-P and ACE-Asia field experiments. *Air Pollution Modelling and Its Application*, XV, 527–528, 2002.
- Yamashita, K., & Sato, J. (2005). Study on the perspective of acid deposition monitoring network in East Asia. *Niigata Rikagaku*, 30, 33–43, (in Japanese).
- Yienger, J. J., & Levy II, H. (1995). Global inventory of soil-biogenic NO_x emissions. *Journal of Geophysical Research*, 100, 11447–11464.

European Critical Loads of Cadmium, Lead and Mercury and their Exceedances

J. Slootweg · J.-P. Hettelingh · M. Posch ·
G. Schütze · T. Spranger · W. de Vries ·
G. J. Reinds · M. van 't Zelfde ·
S. Dutchak · I. Ilyin

Received: 17 June 2005 / Accepted: 12 February 2006 / Published online: 30 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Critical loads of cadmium, lead and mercury were computed by 18 countries of the LRTAP Convention. These national data were collated into a single database for the purpose of identifying sensi-

tive areas in Europe. Computing exceedances, i.e. comparing the critical loads to atmospheric deposition, shows that cadmium was not a widespread risk in 2000, that the risk from lead deposition has decreased since 1990 but was still widespread in 2000, and that the risk from mercury remains high without much change from 1990 to 2000 in most of the countries.

J. Slootweg · J.-P. Hettelingh (✉) · M. Posch
Coordination Centre for Effects, Netherlands
Environmental Assessment Agency (MNP),
P.O. Box 303, 3720 AH Bilthoven, The Netherlands
e-mail: j.p.hettelingh@mnnp.nl

G. Schütze
OEKO-DATA,
Hegermuehlenstrasse 58,
15344 Strausberg, Germany

T. Spranger
Umweltbundesamt (UBA),
P.O. Box 1406, 6813 Dessau, Germany

W. de Vries · G. J. Reinds
Alterra, Wageningen University
and Research Centre (WUR),
P.O. Box 47, 6700 AA Wageningen, The Netherlands

M. van 't Zelfde
Institute of Environmental Sciences (CML),
Leiden University,
P.O. Box 9518, 2300 RA Leiden, The Netherlands

S. Dutchak · I. Ilyin
EMEP/MSC – East,
Ul. Arhitektor Vlasov 51,
117 393 Moscow, Russian Federation

Keywords atmospheric deposition · critical loads · heavy metals · exceedances · LRTAP Convention

1 Introduction

Critical loads of cadmium (Cd), lead (Pb) and mercury (Hg) are derived for European ecosystems using human and environmental endpoints in the framework of activities of the Coordination Centre for Effects (CCE) of the ICP M&M under the Convention on Long-range Transboundary Air Pollution (LRTAP). A methodology was developed under the LRTAP Convention and published in the Mapping Manual (UBA, 2004). This paper summarizes the methodology to assess critical loads of Cd, Pb, and Hg and provides an overview of the risk that deposition of these metals causes. A complete description of the results can be found in Slootweg, Hettelingh, Posch, Dutchak, and Ilyin (2005).

2 Methodology

The critical load of a metal is its highest total input rate from anthropogenic sources to an ecosystem, below which harmful effects on human health, or ecosystem structure and function will not occur over the long-term, according to present knowledge. The critical load is derived with a biogeochemical model, assuming steady-state for the metal fluxes as well as chemical equilibrium consistent with concepts of sustainability. The concentrations in these fluxes are set to thresholds (critical limits), below which significant harmful effects on human health or specified sensitive elements of the environment do not occur.

Critical loads of cadmium, lead and mercury were calculated addressing either ecotoxicological effects on aquatic and terrestrial ecosystems or human health effects. Table 1 presents some possible effects of the three metals that were considered for the critical load assessment.

For simplicity, and consistency with the steady-state mass balance used for nitrogen and acidity critical loads, internal metal cycling within ecosystems is ignored. Weathering inputs of metals are also neglected due to 1) low weathering inputs and 2) high uncertainties of respective calculations.

2.1 Terrestrial Ecosystems

For terrestrial ecosystems (effects 1, 2 and 3 in Table 1) the critical load of a metal equals the sum

of tolerable net metal uptake by plants and metal leaching:

$$CL(M) = M_u + M_{le(crit)} \quad (1)$$

where:

- $CL(M)$ critical load of metal M ($\text{g ha}^{-1} \text{a}^{-1}$)
 M_u net metal uptake in harvestable parts of plants under critical load conditions ($\text{g ha}^{-1} \text{a}^{-1}$)
 $M_{le(crit)}$ critical leaching flux of metal M from the considered soil layer ($\text{g ha}^{-1} \text{a}^{-1}$), whereby only the vertical flux is considered.

The soil depth, for which critical load are calculated, depends on the receptor and the ecosystem type. The net uptake of metals by plants “under critical load conditions” is calculated as {production of harvestable biomass} $\times$ {metal concentration in the harvested parts}. For most plant species the uptake cannot be related to a critical concentration in soil or soil solution, because respective reliable transfer functions are missing. An exception is the relationship of Cd in soil solution to Cd in wheat grains. This transfer function is used to derive a critical concentration in the soil solution from a critical limit for Cd in wheat, while the uptake is calculated by grain production times this critical limit (0.1 mg kg^{-1} fresh weight in the grain), aiming at critical loads related to human health.

The critical leaching is calculated from the water flux percolating through the soil (soil drainage water) and a critical concentration in this flux. Critical total

Table 1 Overview of indicators used in the computation of critical thresholds

Receptor Ecosystem	Endpoints	Heavy metals of concern	Land cover types to be considered	Indicator/critical limit	Effect number
Terrestrial	Human health	Cd, Pb, Hg	All ecosystems	Total concentration in soil water below the rooting zone (to protect ground water)	1
		Cd, Pb, Hg	Arable land	Content in food, fodder and crops	2
		Cd, Pb, Hg	Grassland	Content in grass and animal products (cows, sheep)	
	Ecosystem functions	Cd, Pb	Arable land, grassland, non-agricultural	Free ion concentration in view of effects on soil micro-organisms, plants and invertebrates	3
		Hg	Forest soils	Total concentration in humus layer in view of effects on soil micro organisms and invertebrates	
Aquatic	Ecosystem functions	Cd, Pb, Hg	Freshwaters	Total concentration in view of effects on algae, crustacea, worms, fish, top predators	4
	Human health	Hg	Freshwaters	Concentration in fish	5

concentrations of Cd, Pb and Hg in the soil drainage water depend on the target to be protected. These values are derived from receptor-specific critical limits (see Table 1) which are (for details see De Vries et al., 2004; UBA, 2004):

- Critical Cd contents in wheat grains in view of human health effects through intake of plant products (see above).
- Critical metal concentrations in ground water (Cd, Pb, Hg) in view of human health effects through intake of drinking water. The guidance values of the WHO (2004) can directly be used.
- Critical concentrations of free metal ions (FMI) in soil solution (Cd, Pb) in view of ecotoxicological effects on soil micro-organisms, plants, and invertebrates. FMI must be converted to the total concentration in soil drainage water by using a chemical speciation model. Here pH-dependent critical FMI concentration is used, based on an evaluation of NOEC (*No Observable Effect Concentration*) soil data combined with a transfer function relating the critical concentration in solid soil to that in soil solution. Only data sets were used in which the needed soil properties to apply those functions (pH and organic matter content) were available.
- Critical Hg concentration in soil organic matter (0.5 mg Hg/kg organic matter) in view of ecotoxicological effects on soil micro-organisms and invertebrates in the forest floor. Soil Hg concentration can be converted to a total Hg concentration in soil drainage water by using a transfer function based on dissolved organic matter concentration in the soil solution.

2.2 Aquatic Ecosystems

As with terrestrial ecosystems, the critical load of Cd and Pb for freshwaters (effect 4 in Table 1) is given by Eq. 1 where M_u is the average net uptake in the catchment ($\text{g ha}^{-1}\text{a}^{-1}$) and the leaching has to be replaced by critical outflow of metal from the whole catchment ($\text{g ha}^{-1}\text{a}^{-1}$). A retention term can be added to the basic equation, in particular in calculations for lakes, if the information is available. Neglecting this term leads to a more conservative estimate.

The critical dissolved concentration of Cd (0.38 mg m^{-3}) in the outflow is based on the EU

risk assessment for cadmium metal (EC, 2003). The value for Pb (11 mg m^{-3}) is based on Crommentuijn, Polder, and Van de Plassche (1997). These concentrations have to be converted into total concentrations, accounting for metals bound to suspended particles.

A different approach was used to calculate critical concentration levels of Hg in atmospheric precipitation, to protect against effect 5 (Table 1). This approach aims at the protection of fish used for human food consumption. The recommended critical limit for Hg is 0.3 mg kg^{-1} (fresh weight). Using a 1-kg pike (*Esox lucius*) as a standard receptor (to which Hg concentrations in other organisms can be related) the Hg concentration in fish flesh is related to the mean Hg concentration in precipitation at a given site and the critical level of atmospheric pollution is thus calculated as follows:

$$[\text{Hg}]_{\text{Prec(crit)}} = [\text{Hg}]_{\text{Pike(crit)}} / (\text{TF}_{\text{HgSite}} \cdot c_{\text{bp}}) \quad (2)$$

where:

$[\text{Hg}]_{\text{Prec(crit)}}$	critical Hg concentration in precipitation (ng l^{-1})
$[\text{Hg}]_{\text{Pike(crit)}}$	critical Hg concentration in the flesh of 1-kg pike (0.3 mg kg^{-1} fresh weight)
$\text{TF}_{\text{HgSite}}$	site-specific transfer function (l kg^{-1} fresh weight) referring to the transfer of atmospheric Hg to fish flesh in a watershed at steady state
c_{bp}	$10^{-6} \text{ mg ng}^{-1}$, factor for appropriate conversion of units.

Information on the critical loads methodology of heavy metals can be obtained from the Manual of the ICP Modelling & Mapping (UBA, 2004). Details of the methodology are described in a separate background document (De Vries et al., 2004). In principle the countries were encouraged to use national input data to calculate critical loads. The Manual provides default values, if own data are missing.

3 Results

3.1 Critical Loads

Altogether, 18 countries submitted critical loads of heavy metals. Critical loads of cadmium, lead and mercury were computed by 17, 17, and 10 countries,

respectively. However not all countries addressed all effects, as is shown in Table 2. It shows that most countries computed critical loads for effects 1 and 3.

The European synthesis of the country submissions was done as follows. For each ecosystem the minimum critical load of health effects (effects 1, 2) was taken. The same was done for ecosystem effects (effects 3, 4). Then for each EMEP50 grid cell and for each metal, the fifth percentile of the distribution of these minimum critical loads is calculated for health effects, and ecosystem effects separately. Figure 1 shows the fifth percentile of the minimum critical loads for human health (left) and ecosystem health (right) of Cd (top), Pb (middle) and Hg (bottom). Red areas indicate most sensitive areas.

Effect 5 (not shown here) is treated separately because it is not associated with a critical deposition but with a critical concentration in precipitation. In addition, only three countries (Finland, Sweden and Belgium) submitted critical loads for this effect. It turns out (Slootweg et al., 2005) that the distribution of critical concentrations roughly lies between 0.5 and 5 ng l⁻¹.

3.2 Critical Load Exceedances

Depositions were computed with a long-range atmospheric dispersion model by the EMEP Meteorological Synthesizing Centre East under the LRTAP Convention. The methods used are described in Ilyin and Dutchak (2005).

Depositions were compared to critical loads to identify areas where ecosystems are at risk, i.e. where deposition exceeds critical loads. Tables 3 and 4 show that the risks of effects of lead are more widespread than those of cadmium.

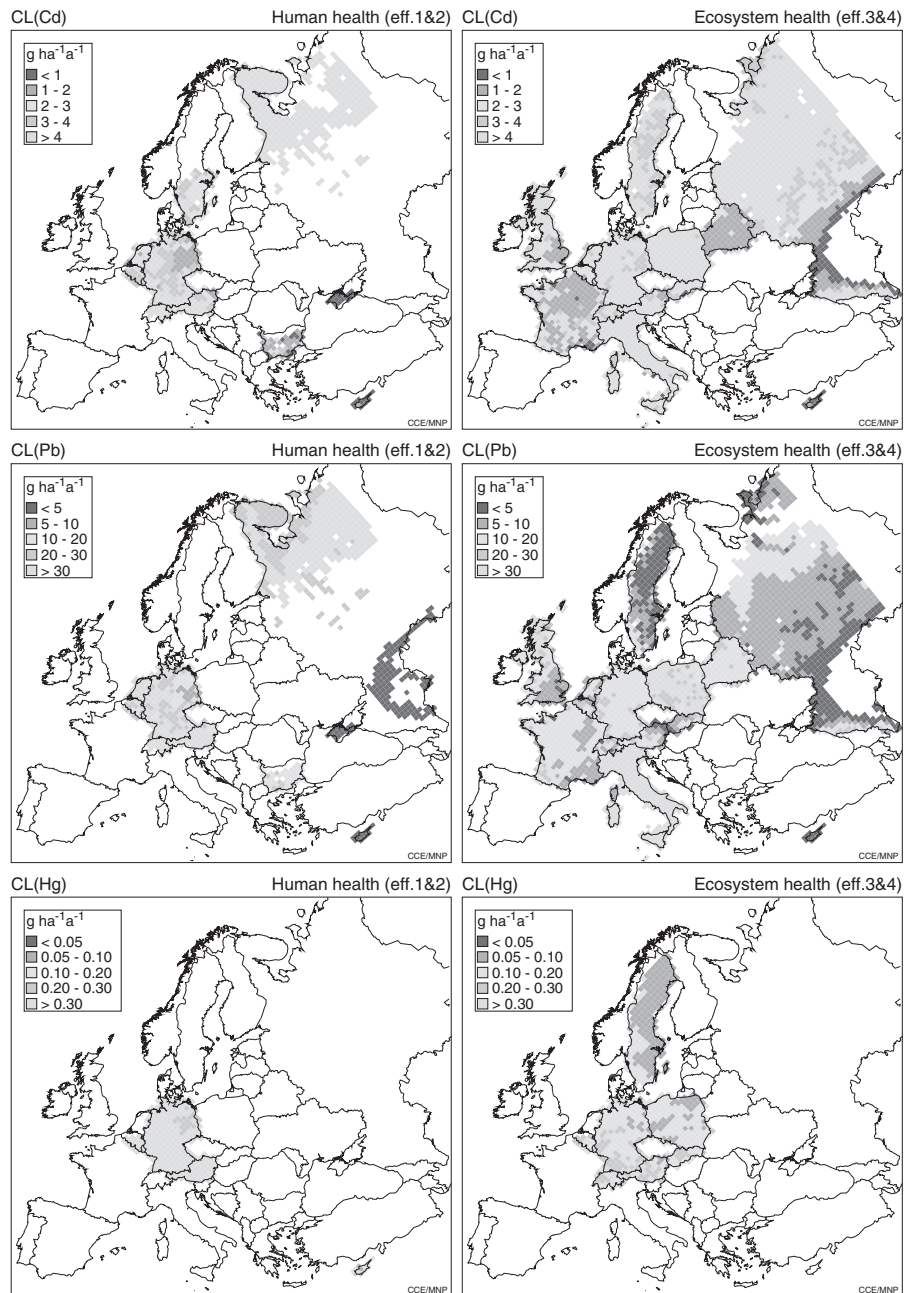
The area of excess deposition of Pb in 2000 is strongly reduced in comparison to 1990 (Tables 3 and 4). In Europe 33.8 % of the ecosystem area in 1990 was subjected to excess deposition of Pb for human health effects, which was reduced to 8.3% in 2000 (Table 3). The risk for ecosystem effects of Pb dropped from 65.7% in 1990 to 28.7% in 2000 (Table 4).

A preliminary analysis of the risk of cadmium and lead caused by agricultural practices was conducted on data available for a few countries, i.e. Austria, Germany, Italy, Sweden, The Netherlands and the

Table 2 Overview of available national data on critical loads of cadmium, lead and mercury for the five effects

Country	Country code	Effect number (Table 1)											
		Cd				Pb				Hg			
		1	2	3	4	1	2	3	4	1	3	5	
Austria	AT	x	x	x		x		x		x	x		
Belarus	BY			x				x					
Belgium	BE	x		x	x	x		x	x	x	x	x	
Bulgaria	BG	x				x							
Cyprus	CY	x	x	x		x		x		x			
Czech Republic	CZ	x				x				x			
Finland	FI												x
France	FR			x				x					
Germany	DE	x	x	x		x		x		x	x		
Italy	IT			x				x					
The Netherlands	NL	x	x	x		x		x					
Poland	PL			x				x			x		
Russia	RU	x		x		x		x					
Slovakia	SK			x				x			x		
Sweden	SE		x	x				x			x	x	
Switzerland	CH	x		x		x		x			x		
Ukraine	UA		x				x						
UK	GB			x				x					
Total	18	10	6	14	1	10	1	14	1	6	7	3	

Fig. 1 Critical loads of cadmium (*top*), lead (*middle*) and mercury (*bottom*) showing maximum allowable atmospheric depositions (*see shadings*) to protect 95% of the ecosystems from risks for human health (*left*) and ecosystem health (*right*). Red and blue shaded areas indicate the most and least sensitive areas, respectively



Ukraine. This analysis revealed that agricultural input of Cd without atmospheric input exceeds critical loads in only one grid cell in Germany. Added to atmospheric deposition, Cd critical loads of agricultural ecosystems in four German grid cells turn out to be exceeded. However, the critical loads of Pb are exceeded by agricultural inputs alone in Austria, the Netherlands and the Ukraine, including large parts of Germany when atmospheric depositions are added.

Critical concentrations in rainwater (effect 5) are exceeded in nearly all grid cells for which data was provided.

4 Conclusions

Critical loads of cadmium (Cd), lead (Pb) and mercury (Hg) were computed by 17, 17, and 10 countries, respectively. The methodology used for calculating critical loads of heavy metals has been

Table 3 Percentage of national ecosystem areas that are at risk of health effects in countries that submitted critical loads of cadmium, lead and/or mercury

Country	Cadmium (Cd)			Lead (Pb)			Mercury (Hg)		
	Eco area (km ²)	1990 at risk (%)	2000 at risk (%)	Eco area (km ²)	1990 at risk (%)	2000 at risk (%)	Eco area (km ²)	1990 at risk (%)	2000 at risk (%)
AT	61,371	0.0	0.0	61,371	24.0	0.0	61,371	0.0	0.0
BE	5,228	0.0	0.0	5,228	62.3	18.2	5,228	22.7	6.1
BG	48,330	42.0	14.8	48,330	99.9	77.2	–	–	–
CH	2,200	0.0	0.0	2,218	72.0	2.3	–	–	–
CY	7,973	1.3	0.8	7,973	74.1	70.4	7,973	4.2	4.1
CZ	25,136	1.1	0.5	25,136	93.1	19.9	25,136	7.4	1.9
DE	290,003	1.4	0.1	290,003	79.0	7.4	290,003	17.9	4.8
NL	19,471	0.1	0.0	19,471	89.2	0.1	–	–	–
RU	425,425	0.0	0.0	650,575	3.3	2.5	–	–	–
SE	22,050	0.0	0.0	–	–	–	–	–	–
UA	18,002	0.0	0.0	18,002	91.6	41.4	–	–	–
EU25	431,232	1.1	0.1	409,182	71.8	8.1	389,711	14.2	3.9
Europe	925,190	2.7	0.8	1,128,308	33.8	8.3	389,711	14.2	3.9

carefully reviewed and is documented in the Mapping Manual of the ICP on Modelling and Mapping. The methodology enabled the assessment of ecosystem specific critical loads to protect human or environmental health. These critical loads were compared to preliminary computations of ecosystem specific deposition of the respective metals in 1990 and 2000. The

robustness of deposition results can not yet well be established due to the many uncertainties. Bearing these uncertainties in mind, atmospheric deposition of Cd did not cause widespread risk in 2000, that the risk of Pb deposition decreased after 1990 but was still widespread in 2000 and, finally, that the risk caused by Hg did not change much from 1990 to 2000 in

Table 4 Percentage of national ecosystem areas that are at risk of ecosystem effects in countries that submitted critical loads of cadmium, lead and/or mercury

Country	Cadmium (Cd)			Lead (Pb)			Mercury (Hg)		
	Eco area (km ²)	1990 at risk (%)	2000 at risk (%)	Eco area (km ²)	1990 at risk (%)	2000 at risk (%)	Eco area (km ²)	1990 at risk (%)	2000 at risk (%)
AT	61,371	0.0	0.0	61,371	48.7	11.1	32,601	39.2	11.7
BE	5,237	0.0	0.0	5,237	63.0	12.8	5,228	100.0	83.5
BY	121,128	9.1	0.1	121,128	100.0	10.2	–	–	–
CH	9,411	0.0	0.0	9,393	99.0	24.1	11,611	80.2	44.4
CY	7,973	0.0	0.0	7,973	80.9	78.4	–	–	–
DE	290,003	0.1	0.0	290,003	83.8	9.0	99,866	97.0	59.8
FR	170,638	0.1	0.0	170,638	93.7	9.8	–	–	–
GB	50,075	0.5	0.0	50,075	25.9	6.0	–	–	–
IT	278,128	0.0	0.0	278,128	0.3	0.0	–	–	–
NL	22,314	0.0	0.0	22,314	98.4	21.5	–	–	–
PL	88,383	0.5	0.0	88,383	73.5	14.7	88,383	100.0	99.9
RU	1,393,300	1.1	0.2	1,194,125	70.8	51.0	–	–	–
SE	151,432	0.0	0.0	151,432	60.5	1.9	152,074	56.0	22.9
SK	19,253	2.6	1.1	19,253	52.3	22.6	19,253	99.0	65.3
EU25	1,144,807	0.1	0.0	1,144,807	56.3	7.4	397,405	77.4	51.2
Europe	2,668,646	1.0	0.1	2,469,453	65.7	28.7	409,016	77.4	51.0

most of the countries that provided data on mercury. Agricultural input of Cd causes exceedance in a single grid cell. For Pb fertilisation alone *does* exceed critical loads, especially in the Netherlands. Added to atmospheric deposition, however, the critical load of Pb is exceeded also in central Germany.

References

- Crommentuijn, T., Polder, M. D., & Van de Plassche, E. J. (1997). Maximum permissible concentrations and negligible concentrations for metals, taking background concentrations into account, Report 601501001 (157 pp) Bilthoven, The Netherlands: National Institute for Public Health and the Environment.
- De Vries, W., Schütze, G., Loftis, S., Tipping, E., Meili, M., Römkens, P. F. A. M., et al. (2004). Calculation of critical loads for cadmium, lead and mercury, Alterra Report 1104, Wageningen, The Netherlands, 143 pp.
- EC (2003). Risk Assessment cadmium metal, CAS-No.: 7440-43-9, EINECS No 231-152-8, Draft risk assessment report in accordance with council regulation EEC 793/93.
- Ilyin, I., & Dutchak, S. (2005). Deposition modelling for heavy metals (pp. 39–60). In Slootweg et al. (Eds.) (op. cit.).
- Slootweg, J., Hettelingh, J.-P., Posch, M., Dutchak, S., & Ilyin, I. (Eds.) (2005). Critical loads of cadmium, lead and mercury in Europe, CCE-MSCE Collaborative report. Bilthoven, The Netherlands: Netherlands Environmental Assessment Agency, <http://www.mnp.nl/cce>.
- UBA (2004). Manual on methodologies and criteria for modelling and mapping of critical loads and levels and air pollution effects, risks and trends, UBA-Texte 52/2004. Berlin, Germany: Federal Environmental Agency, <http://www.icpmapping.org>.
- WHO (2004). Guidelines for drinking water quality, 3rd edn (vol 1), recommendations. Geneva : World Health Organisation.

Critical Loads and Dynamic Modelling to Assess European Areas at Risk of Acidification and Eutrophication

J.-P. Hettelingh · M. Posch · J. Slootweg ·
G. J. Reinds · T. Spranger · L. Tarrason

Received: 17 June 2005 / Revised: 2 December 2005 / Accepted: 17 December 2005 / Published online: 30 January 2007
© Springer Science + Business Media B.V. 2007

Abstract European critical loads and novel dynamic modelling data have been compiled under the LRTAP Convention by the Coordination Centre for Effects. In 2000 9.8% of the pan-European and 20.8% of the EU25 ecosystem area were at risk of acidification. For eutrophication (nutrient *N*) the areas at risk were 30.1 and 71.2%, respectively. Dynamic modelling results reveal that 95% of the area at risk of acidification could recover by 2030 provided acid deposition is reduced according to present legislation. Insight into the timing of effects of exceedances of critical loads for nutrient *N* necessitates the further development of dynamic models.

Keywords acid deposition · critical loads · dynamic modelling · exceedances · LRTAP Convention

1 Introduction

The critical load concept has been developed in Europe since the mid-1980s, mostly under the auspices of the 1979 Convention on Long-range Transboundary Air Pollution (LRTAP). European data bases and maps of critical loads have been instrumental in formulating effects-based Protocols to the LRTAP Convention, such as the 1994 Protocol on Further Reduction of Sulphur Emissions (the ‘Oslo Protocol’) and the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (the ‘Gothenburg Protocol’). The methods and maps used to support these agreements are described in Hettelingh, Posch, De Smet, Downing (1995) and Hettelingh, Posch, De Smet (2001).

In 2005, European data on critical loads for acidification and eutrophication was updated, including a novel database on dynamic modelling outputs. By definition, critical loads do not provide any information on time scales of recovery or damage. Therefore, the use of dynamic models has been recognized as an important part of the work programme under the LRTAP Convention. Of particular interest are the ecosystems where depositions exceeded or continue to exceed critical loads.

J.-P. Hettelingh (✉) · M. Posch · J. Slootweg
Coordination Centre for Effects, Netherlands
Environmental Assessment Agency (MNP),
P.O. Box 303, NL-3720 AH Bilthoven, The Netherlands
e-mail: j.p.hettelingh@mnpl.nl

G. J. Reinds
Alterra, Wageningen University
and Research Centre (WUR),
P.O. Box 47, NL-6700 AA Wageningen, The Netherlands

T. Spranger
Umweltbundesamt (UBA),
P.O. Box 1406, 6813 Dessau, Germany

L. Tarrason
EMEP/MS-C-W, Norwegian Meteorological Institute,
P.O. Box 43, Blindern,
0313 Oslo, Norway

This paper focuses on the dynamic modelling results. It also summarizes the European critical load database and provides information on the extent of their exceedances.

2 Materials and Methods

2.1 Critical Loads

Most of the European critical loads are computed with the Simple Mass Balance (SMB) (or related) models (Sverdrup & De Vries, 1994), applied by the Coordination Centre for Effects (CCE) and a network of 25 National Focal Centres associated with the Modelling and Mapping Programme under the LRTAP Convention. The methods are described in a Mapping Manual (UBA, 2004); they have not significantly changed since they were summarized in Hettelingh et al. (2001).

Critical loads are compared to depositions of sulphur and nitrogen, computed with the EMEP ‘unified’ long-range atmospheric transport and dispersion model (Tarrasón et al., 2005), to compute the percentage of ecosystem area exceeded or the exceedance amounts in the $50 \times 50 \text{ km}^2$ EMEP grid cells covering Europe. Exceedances are expressed as so-called average accumulated exceedance, the area-weighted mean of individual critical load exceedances within a grid cell (see Posch, Hettelingh, & De Smet, 2001).

2.2 Dynamic Modelling

Models to determine critical loads consider only the steady-state condition for a prescribed chemical and biological response. Dynamic models, on the other hand, attempt to estimate the time required for a new steady state to be achieved. Over the past 20 years dynamic soil-chemical models have been applied to a large number of individual sites, and there are also several examples of earlier applications on a regional scale. In view of the broad published knowledge on dynamic modelling, a methodological summary will not be attempted here; a description of the most important processes captured in dynamic models can be found in UBA (2004).

In critical load assessments, two cases can be distinguished when comparing critical loads to deposition: (1) the deposition is below critical loads, and

(2) the deposition is greater than critical loads. In the first case there is no apparent problem; in the second case there is, by definition, an increased risk of damage to the ecosystem, and deposition should be reduced. However, it is often assumed that reducing deposition to critical loads immediately removes the risk of ‘harmful effects,’ i.e. the chemical criterion that links the critical load to the biological effects, immediately attains a non-critical value. But the reaction of soils, especially their solid phase, to changes in deposition is delayed by finite buffers, such as the cation exchange capacity. It might take decades or even centuries, before steady state is reached. Therefore, dynamic models are needed (a) to estimate the time involved in attaining a certain chemical state in response to emission scenarios, or conversely (b) to estimate so-called target loads – deposition levels to be achieved through sufficient emission reductions – at which recovery will occur in a specified year (the target year). In this paper results for the target years 2030 and 2100 are reported.

Figure 1 summarises the possible development of a (soil) chemical and biological variable in response to a ‘typical’ temporal deposition pattern. Five stages can be distinguished (see Posch, Hettelingh, & Slootweg, 2003):

- *Stage 1:* Deposition was and is below the critical load (CL), e.g. in the pre-industrial era, and the chemical and biological variables do not violate their respective criteria.
- *Stage 2:* Deposition is above the CL, but (chemical and) biological criteria are not violated because there is a time delay before this happens. Therefore, no damage is likely to occur at this stage. The time between the first exceedance of the CL and the first violation of the biological criterion (the first occurrence of actual damage) is termed the ‘Damage Delay Time’ ($DDT = t_3 - t_1$).
- *Stage 3:* The deposition is above the CL and both the chemical and biological criteria are violated. Measures are required to avoid a (further) deterioration of the ecosystem status.
- *Stage 4:* Deposition is below the CL, but the criteria are still violated and thus recovery has not yet occurred. The time between the first non-exceedance of the CL and the subsequent non-violation of both criteria is termed the ‘Recovery Delay Time’ ($RDT = t_6 - t_4$).

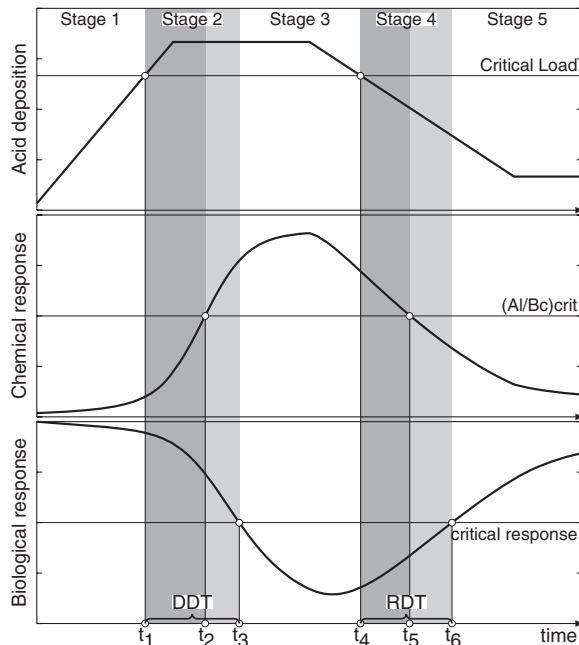


Fig. 1 ‘Typical’ past and future development of the acid deposition (*top*) and its effects on a soil chemical variable (*middle*) and the corresponding biological response (*bottom*) in comparison to the critical values of those variables. The delay between the (non-)exceedance of the critical load, the (non-)violation of the critical values is indicated in *grey shadings*, highlighting the Damage Delay Time (DDT) and the Recovery Delay Time (RDT) of the system (from Posch et al., 2003)

- **Stage 5:** Deposition is below the CL and both criteria are no longer violated; and only at this stage can the ecosystem be considered to have recovered. Stages 2 and 4 can each be subdivided into two sub-stages: Chemical delay times ($DDT_c = t_2 - t_1$ and $RDT_c = t_5 - t_4$; dark grey in Fig. 1) and (additional) biological delay times ($DDT_b = t_3 - t_2$ and $RDT_b = t_6 - t_5$; light grey).

Dynamic modelling was carried out with a deposition path resulting from the Current Legislation (CLE) emissions scenario, which implements the Gothenburg Protocol and the National Emission Ceilings Directive of the European Union.

3 Results

3.1 European Critical Loads and Exceedances

Figure 2 shows maps of critical loads for different ecosystem classes, based on national contributions from 25 countries. For countries that never submitted

critical loads, data from the European background database have been used (Posch, Slootweg, & Hettelingh, 2005).

The maps show for every EMEP grid cell the 5th percentile of the critical load for acidification for all ecosystems combined (top-left), forest ecosystems (top-right), semi-natural vegetation (bottom-left) and aquatic ecosystems. Low critical loads below $200 \text{ eq ha}^{-1} \text{ yr}^{-1}$ (red shaded) occur mostly in the northern parts of Europe. While in Norway only surface waters are sensitive, in Sweden both forest and aquatic ecosystems have low critical loads. In the United Kingdom most of the sensitive ecosystems are classified as semi-natural vegetation. Similar maps for the critical loads for eutrophication (not shown here; but see Posch et al., 2005) show values for the 5th percentile below $400 \text{ eq ha}^{-1} \text{ yr}^{-1}$ in large parts of Europe.

Using EMEP depositions for the year 2000, maps of exceedances of critical loads for all ecosystems are shown in Fig. 3. In Europe 8.5% of the ecosystem area is at risk of acidification (and 17.5% for the EU25), whereas for eutrophication the area with exceedances covers 28.5% of the ecosystem area (65.2% for the EU25). The areas where exceedances occur are of most interest for the application of dynamic models.

3.2 Dynamic Modelling Results

Table 1 summarizes the dynamic modelling results. Most relevant is the ecosystem area where critical loads are exceeded. Using the data from Fig. 3, this area turns out to be $579,975 \text{ km}^2$. The area for which dynamic modelling has been carried out is $683,237 \text{ km}^2$ (see column 2 in Table 1), and this area includes most of that exceeded area. Of the area in column 2, $168,661 \text{ km}^2$ turned out *not to be safe* (column 3), meaning that the critical loads are exceeded or that the critical limit is violated (or both). All following columns are expressed as percentages of this ‘non-safe’ area.

Column 4 shows the percentage of the area for which a Recovery Delay Time (RDT) can be computed under the CLE scenario. This is the case for ecosystems for which the critical load is at present no longer exceeded, but the critical limit is still violated (see Fig. 1). It shows that in Europe 29.2% of the area, which is not safe at present, would recover

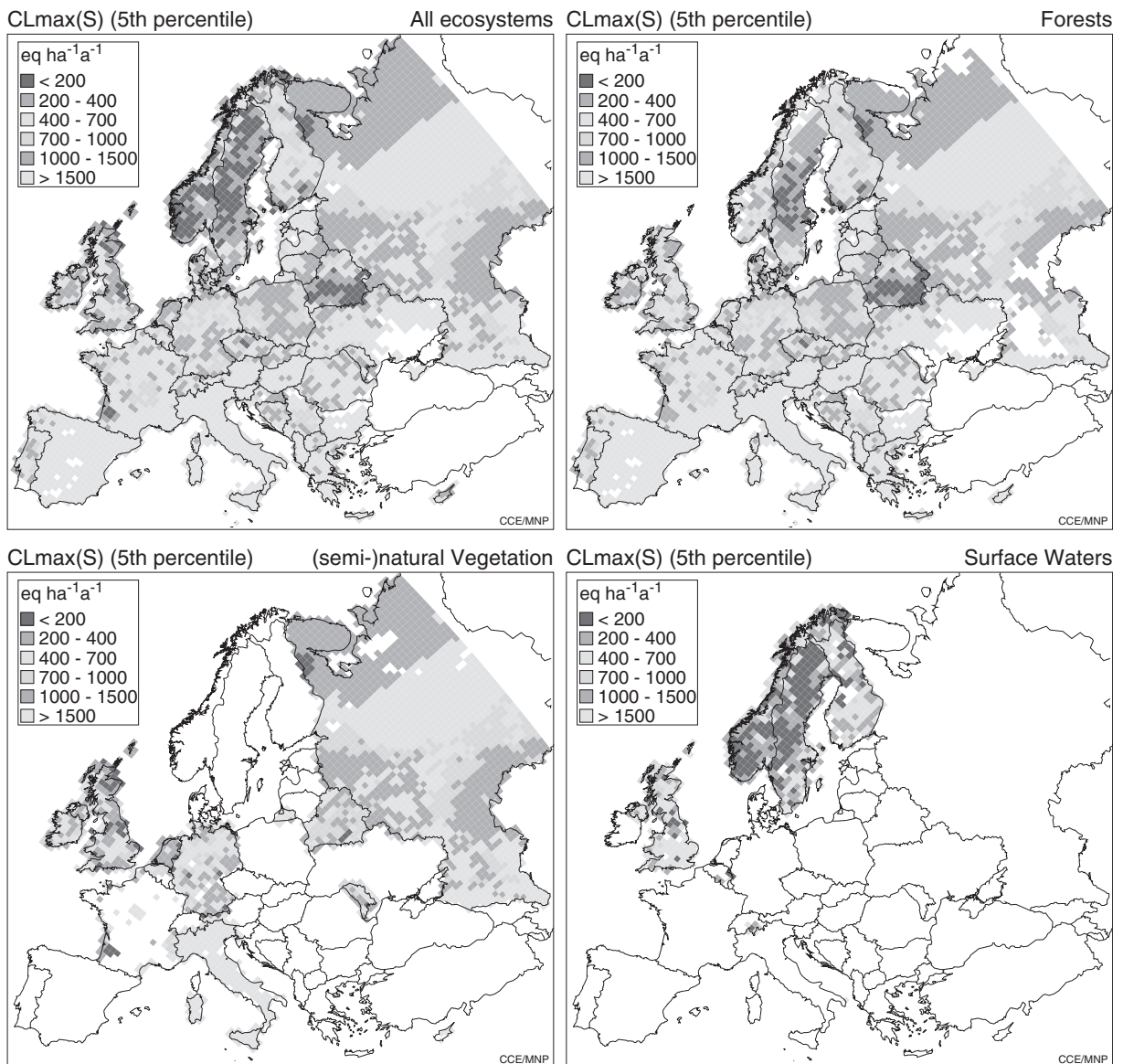


Fig. 2 The 5th percentile of the critical loads for acidification for all ecosystems (*top left*), forests (*top right*), semi-natural vegetation (*bottom left*) and surface waters

sometime in the future without further emission reductions. In fact, CLe depositions cause 20.2% to recover already before 2030 (see column 6), while by 2100 they will lead to a recovery of 22.3% of the ecosystem area (column 10). Comparing column 10 to 4, we conclude that $29.2 - 22.3 = 6.9\%$ of the area which is not safe at present would recover only after 2100. Deposition levels would need to be reduced to enlarge the area that recovers before 2100 or to bring closer the year of recovery. By how much deposition has to be reduced to obtain the target load, depends on

the year (the target year) in which recovery should occur. The percentage of the European area for which target loads can be computed in 2030 and 2100 are provided in columns 8, and 12, respectively.

Column 5 gives the percentage of the area for which a Damage Delay Time (DDT) can be computed (see Fig. 1). This is the case in areas where the critical load is already exceeded, but the critical limit is not yet violated. In Europe 23.4% of the non-safe ecosystem area (column 3) will be damaged in the future under the CLe scenario.

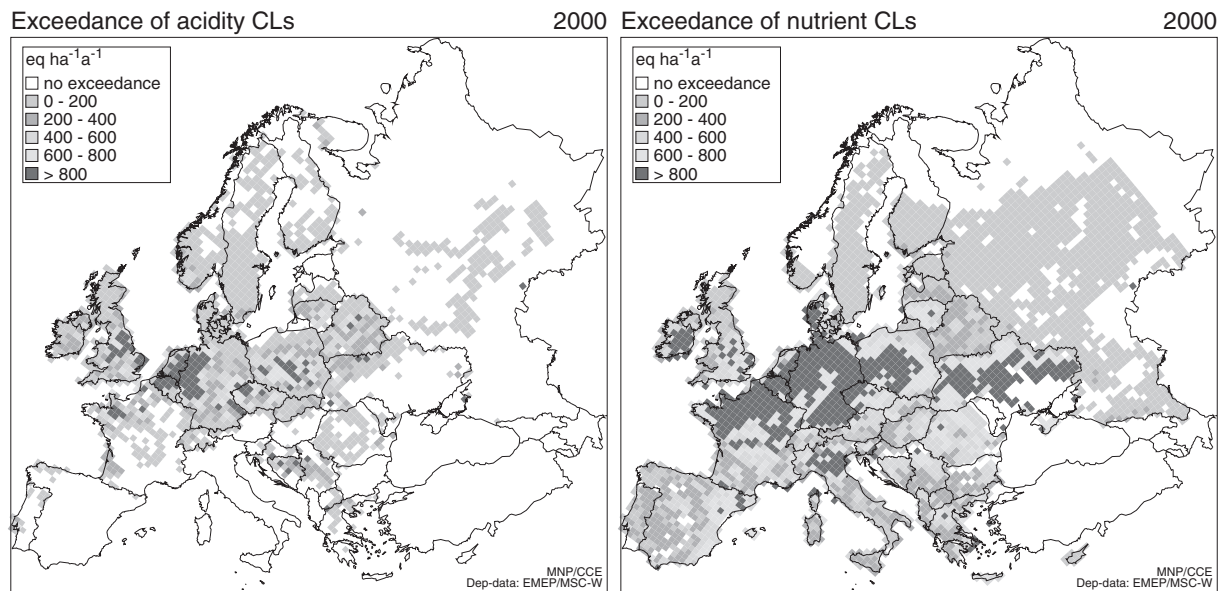


Fig. 3 Average accumulated exceedance for all ecosystems in the year 2000 of acidity (*left*) and nutrient N critical loads. White areas indicate non-exceedance or no data

Column 6 gives the percentage of the area that will be safe (critical limit not violated *and* deposition not exceeding critical loads) in 2030 under the CLe scenario, i.e. 20.2%. Column 7 lists the percentages of areas at risk (not safe) where target loads for recovery in 2030 equal critical loads, i.e. 24.2% in Europe. Target loads lower than critical loads (column

8) are found for 50.7% of the ecosystem area. The area for which no target loads can be found, i.e. for which even zero deposition would not lead to recovery in 2030, covers 5% in Europe (column 9). We conclude that the area which is – and would become – safe in 2030 (columns 6+7+8) is about 95% of the areas which are not safe now (column 3).

Table 1 Summary of dynamic modelling results (see text for explanations)

1	2	3	4	5	6	7	8	9	10	11	12	13
Country	DynMod	Non-safe	RDT	DDT	Target year 2030				Target year 2100			
–	km ²	km ²	%	%	Safe	TL = CL	TLs	n.f.	Safe	TL = CL	TLs	n.f.
AT – Austria	35,745	334	31.0	53.4	31	36.4	32.6	0	31	36.4	32.6	0
BG – Bulgaria	47,887	0	0	0	0	0	0	0	0	0	0	0
CH – Switzerland	11,612	2,650	14.8	0	9	24.5	63.8	2.7	13.7	26.3	59.9	0
CZ – Czech Republic	11,178	8,004	27.1	14.9	22.2	13.6	59.2	4.9	25	13.6	60.7	0.7
DE – Germany	104,195	57,639	23.7	16.7	21.6	17.2	58.7	2.5	22.7	16.5	59.4	1.5
FR – France	180,074	21,510	38.9	15.3	35.8	16	43.5	4.7	38.6	16	44.1	1.3
GB – United Kingdom	1,190	401	83.8	0	16.2	7	59.2	17.6	16.2	16.4	53.9	13.6
HU – Hungary	10,448	0	0	0	0	0	0	0	0	0	0	0
IE – Ireland	8,936	1,542	42.3	41.7	42.3	44.3	13.4	0	42.3	44.5	13.1	0
IT – Italy	125,878	0	0	0	0	0	0	0	0	0	0	0
NL – Netherlands	6,052	3,984	1.3	4.3	0	14.2	71.7	14.2	1.3	14.3	84.4	0
NO – Norway	20,535	12,183	76.5	0	0	7.5	87.6	4.9	0	13	86.4	0.7
PL – Poland	88,383	48,739	19.8	47.8	19.2	47.5	32	1.2	19.8	46.7	33.5	0
SE – Sweden	31,124	11,676	38.5	8.8	13.9	2.4	52.3	31.4	29.1	2.2	41	27.8
Europe	683,237	168,661	29.2	23.4	20.2	24.2	50.7	5	22.3	24.2	50.8	2.7

Finally, 10–13 provide the analogous information for 2100. Note, that the areas defined as ‘safe’ (columns 6 and 10) increase from 2030 to 2100, whereas the areas for which target loads are not feasible (columns 9 and 13) diminish in the same period. This implies that part of the area that could recover in 2030 by identifying a target load would recover by 2100 under the CLe scenario, i.e. without additional reduction measures.

4 Conclusions and Recommendations

Using depositions for the year 2000 shows that critical loads in 8.5% of the ecosystem area in Europe are exceeded; and for eutrophication this area is even 28.5%. These exceedances imply that those ecosystems are sooner or later at risk of being damaged. To be able to estimate the timing of this damage, dynamic modelling is required. The use of dynamic models of acidification enabled to identify that about 95% of the ecosystems still at the risk of damage in 2010 could recover by 2030 if acid deposition is sufficiently reduced. This includes about 50% of the ecosystems for which reductions even below critical load are required. The high exceedances of critical loads for eutrophication make it desirable to use dynamic models to improve also our knowledge on time delays of damage and recovery caused by excessive inputs of nitrogen.

References

- Hettelingh, J.-P., Posch, M., & De Smet, P. A. M. (2001). Multi-effect critical loads used in multi-pollutant reduction agreements in Europe. *Water, Air and Soil Pollution*, 130, 1133–1138.
- Hettelingh, J.-P., Posch, M., De Smet, P. A. M., & Downing, R. J. (1995). The use of critical loads in emission reduction agreements in Europe. *Water, Air and Soil Pollution*, 85, 2381–2389.
- Posch, M., Hettelingh, J.-P., & De Smet, P. A. M. (2001). Characterization of critical load exceedances in Europe. *Water, Air and Soil Pollution*, 130, 1139–1144.
- Posch, M., Hettelingh, J.-P., & Slootweg, J. (eds.) (2003). Manual for dynamic modelling of soil response to atmospheric deposition. Coordination Center for Effects, RIVM Report 259101012, Bilthoven, Netherlands, 71 pp (<http://www.mnp.nl/cce>).
- Posch, M., Slootweg, J., & Hettelingh, J.-P. (Eds.) (2005). European critical loads and dynamic modelling results, Status Report 2005. Coordination Center for Effects, MNP-Report 259101016, Bilthoven, Netherlands, 167 pp (<http://www.mnp.nl/cce>).
- Sverdrup, H., & De Vries, W. (1994). Calculating critical loads for acidity with the simple mass balance methods. *Water, Air and Soil Pollution*, 72, 143–162.
- Tarrasón, L., Benedictow, A., Fagerli, H., Jonson, J. E., Klein, H., Van Loon, M., et al. (2005). Transboundary acidification, eutrophication and ground level ozone in Europe in 2003, EMEP Status report 1/2005, Norwegian Meteorological Institute, Oslo, Norway. Retrieved from <http://www.emep.int>.
- UBA (2004). Manual on methodologies and criteria for modelling and mapping of critical loads and levels and air pollution effects, risks and trends. Umweltbundesamt, Dessau, Germany. Retrieved from <http://www.icpmapping.org>.

On the Calculation and Interpretation of Target Load Functions

Mattias Alveteg · Liisa Martinson

Received: 17 June 2005 / Revised: 1 February 2006 / Accepted: 12 February 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract In this study critical load functions and target load functions of nitrogen and sulphur deposition with respect to acidity and minimum base cation to aluminium ratio were calculated with the SAFE model using three different averaging strategies: (1) averaging based on current forest generation, (2) averaging based on next generation and (3) averaging based on the entire simulation period. From the results it is evident that although target load calculation and indeed critical load calculation is straight forward, there is a problem in translating a predicted recovery according to the target load calculation back to a site-specific condition. We conclude that a policy strategy for emission reductions that ensures recovery, according to calculated target load functions, is likely to be beneficial from an ecosystem point of view. However, such a strategy may not be sufficient to achieve actual non-violation of the chemical criteria throughout the seasonal or rotational variations. To address this issue we propose a method for calculating dynamic critical loads which ensures that the chosen criteria is not violated.

Keywords acidification · critical loads · modelling · recovery · the SAFE model

1 Introduction

It has long been known that acidifying deposition can lead to adverse effects in soils and waters. As the struggle to decrease acidifying deposition in Europe has been such a success, it is easy to forget how severe the acidification problem was, and was projected to become in Europe. As has been pointed out by e.g. Ågren (2002) the deposition levels in 2010 agreed upon in the Gothenburg protocol (UNECE, 1999) are similar or slightly lower than what was regarded as unreasonable emission reductions in the Stockholm conference in 1972.

One contributing factor to the so far successful reduction of emissions in Europe is the Critical Load concept. The critical load is defined as (Nilsson & Grennfelt, 1988):

A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge

Similar to critical loads (CL) of acidity, the load for which a chemical criteria (such as the base cation to aluminium ratio) will not be violated in the long perspective, a target load can be defined for a site

M. Alveteg (✉)
Department of Chemical Engineering, Lund University,
P. O. Box 124, 221 00 Lund, Sweden
e-mail: Mattias.Alveteg@chemeng.lth.se

L. Martinson
Lund University Center of Sustainability Studies (LUCSUS),
Lund, Sweden
e-mail: Liisa.Martinson@lucsus.lu.se

(Jenkins, Cosby, Ferrier, Larssen, & Posch, 2003; Hettelingh, Posch, & Slootweg, 2005). A target load (TL) is a deposition level at which a site recovers from acidification by a specified target year after which the criteria must remain non-violated. In target load calculations constant or monotonous drivers must be used: If seasonal and rotational variations were to be used in the simulations, the projected future criteria would fluctuate. A site could then be violated e.g. during the early years of each rotation period only, or each summer, and the target load would therefore not be uniquely defined. The constant drivers – nutrient uptake, nutrient cycling and climate – are based on averages, typically over one forest generation. The VSD model (Posch, Hettelingh, & Slootweg, 2003) uses the current rotation period whereas the next rotation period has been used as basis for averaging in the Swedish national data delivery (Bertills et al., 2005) using SAFE (Warfvinge, Falkengren-Grerup, Sverdrup, & Andersen, 1993).

An advantage with evaluating future criteria using constant, rather than varying, nutrient uptake, nutrient cycling and climate, is that the TL-function approaches the CL-function as the target year approaches infinity. The most simple TL-functions are, just as the most simple CL-functions, defined by three numbers (Fig. 1): TL maximum S deposition (TLMaxS), TL minimum N deposition (TLMinN) and TL maximum N deposition (TLMaxN). Because of the requirement that the site must remain non-violated after the target year, a properly cal-

culated TL for a site is also smaller than or equal to the CL for that site.

The results from CL calculations and TL calculations are comparatively easy to communicate: The CL and the TL set limits for acceptable levels of atmospheric deposition (Hettelingh, Slootweg, & Posch, 2004). These limits can in turn be used as basis for negotiations on emission reductions.

However, simple messages such as CL and TL can easily be misinterpreted or over-interpreted: Attempts are sometimes made to falsify the CL concept by comparing with current forest health status, but the time delay between changes in deposition and changes in soil chemistry make such a comparison unreliable, as many researchers have pointed out (e.g. Sverdrup et al., 2005). Furthermore, the calculation of critical loads and target loads requires time-averaged input on atmospheric deposition, climate and nutrient uptake. By removing the naturally occurring and forest management induced variations in key drivers, the actual variation in the chemical criteria is lost and cannot be accounted for. Thus, the comparison with reality, where a forest experiences daily, seasonal and rotational variations, is problematic.

The aim of this article is (1) to illustrate how the choice of averaging method affects TL and CL calculations and (2) to illustrate how the averaging of rotational variations required in critical load and target load calculations makes it difficult to compare exceedance of critical loads and target loads with field measurements.

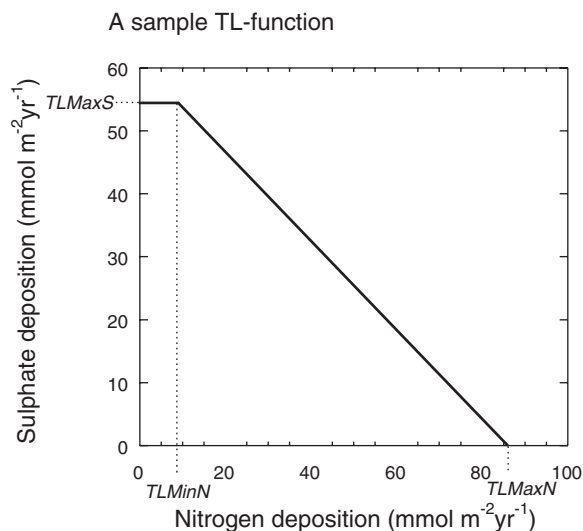


Fig. 1 An example of a TL-function that can be defined by the three numbers TLMaxS, TLMinN and TLMaxN in the same way as a simple CL-function can be defined by CLMaxS, CLMinN and CLMaxN

2 Materials and Methods

Critical loads and target loads were calculated with SAFE (Alveteg, 1998, Warfvinge et al., 1993). As the focus of this article is TL and CL methodology/interpretation rather than evaluation of a specific site, we chose to perform the calculations for the site Söstarad, a Swedish ICP Forest Level II plot, which has been described and modeled with SAFE earlier (see Martinson et al., 2005). The criteria chosen, SAFE being a dynamic multi-layer soil chemistry model, was the minimum molar base cation (Bc) to Al³⁺ ratio in the rooting zone. The implementation year, i.e. the year at which all emission reductions are to be implemented, was chosen as 2020 and was approached linearly from the 2010 deposition levels as projected

by (Schöpp, Posch, Mylona, & Johansson, 2003). In the original application (Martinson et al., 2005) time-series of nutrient uptake and nutrient cycling needed by SAFE were calculated using the MAKEDEP model (Alveteg, Kurz, & Becker, 2002) based on information on current standing biomass and forest management.

Three different methods were chosen for computing the constant nutrient uptake and nutrient cycling required in CL and TL calculations, based on the time-series of the original application:

1. Average based on projections of the next (forthcoming) rotation period, i.e. the period that starts after the harvest (clearcut) of the currently standing biomass.
2. Average based on current rotation period
3. Average based on entire simulation period (1800–2100)

The average calculated using methods 1 through 3 above can be used either for the entire simulation period, i.e. ignoring the dynamic history of a site, or for the future only. If the average is used for the entire simulation period one might either keep the old initial base saturation or recalibrate it using present day measurements of base saturation. Three different ways of using the calculated averages were therefore used:

- A. Average approached linearly between 2000 and 2010
- B. Average approached linearly between 1800 and 1810
- C. Average approached linearly between 1800 and 1810, recalibrating base saturation

It should be noted that variants A through C do not change the future load of acidity and thus do not have any effect on calculated critical loads. These variants might, however, produce different target loads.

All nine simulations thus start with the same steady state chemistry, with the exception that the three C variants start with a different initial base saturation. As the original application only included forest management for the current rotation period at Söstared, MAKEDEP was reapplied before method 2 was applied. It was then assumed that the forest management for the next rotation period will be identical with the current. In our opinion, averaging based on the next rotation period, i.e. method 1, is the most reasonable method since it is the future forest we would like to protect.

Target load functions were calculated for 2030, 2050 and 2100.

3 Results and Discussion

There are several reasons why the averaging method may have a profound effect on calculated TL and CL-functions as is the case with the Söstared site (Fig. 2). Changing averaging method affects nutrient uptake, resulting in different TLMinN: In the SAFE model approach uptake is calculated by the MAKEDEP model. In MAKEDEP a decrease in N deposition often results in a decreased growth i.e. a decrease in nutrient uptake which in turn affects the TLMinN (Table 1). Consequently, the calculated TL and CL functions partly reflect the average nutrient uptake used. Averaging based on the next rotation period, which produces the highest net uptake, results in the highest TL and averaging based on the entire simulation period (method 3) results in the lowest. When interpreting the results of method 3 it should be noted that Söstared was not forested before 1922. Consequently, the average nutrient uptake is much lower with method 3 (averaging between 1800 and 2100) than with the other two methods. The results of method 3 could therefore be taken as an indication of how large effect a change in forest management practice could have on CL and TL functions.

From the results (Fig. 2) one might draw the conclusion that CL and TL can be increased by applying a more intensive forest management practice. In reality, however, this is only partly true. Although an increase in biomass removal may partly solve the problem with high N deposition levels (Akselsson, 2005), such a change also results in an increased removal of base cations, which in turn jeopardize the long term sustainability. To fully address the effect of changes in forest management, however, a process based vegetation model needs to be included in the model setup, which is the case with the FORSAFE model (Wallman, Svensson, Sverdrup, & Belyazid, 2005).

Changing averaging method also affects nutrient cycling and thus how soil chemistry changes with soil depth. The influence of nutrient cycling on TL and CL vary from site to site, the influence being larger the higher up in the soil profile the minimum Bc/Al ratio occurs. The effect the choice of averaging method has on CL and TL functions for Söstared is thus site

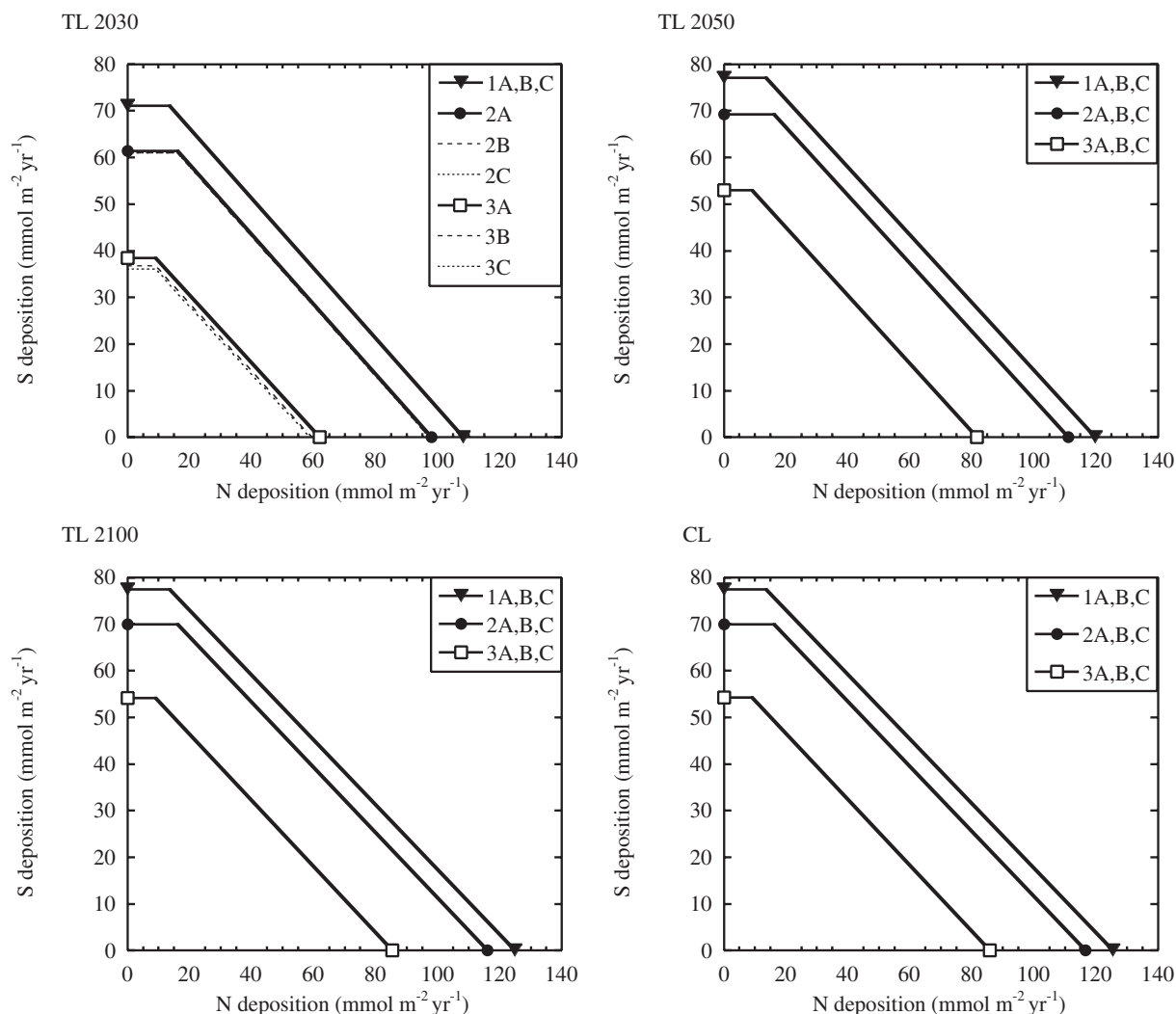


Fig. 2 CL-functions and TL-functions calculated for Söstared. The three methods A, B and C produce essentially identical results except in the TL 2030 calculation, where C gives a slightly lower result than B (lines partly overlap in figure above)

Table 1 The averages resulting from the three different averaging methods

	Method 1	Method 2	Method 3
Net uptake of N (NU_N)	22.0	20.9	11.9
Net mineralization of N (NM_N)	8.4	4.7	2.9
$TL_{minN} = NU_N - NM_N$	13.6	16.2	9.0

Note that method 1 produced the highest values (shown in italics) for net uptake and net mineralization, whereas method 2 produced the highest TL_{minN} .

specific and it is difficult to draw generally applicable conclusions about sites in general. In fact, depending on the relative balance between N and Bc in nutrient cycling it is theoretically possible that a higher nutrient cycling yields lower TL and CL for a site. It should be noted that TL and CL functions also may be calculated by treating the entire soil profile as one homogenous layer. Although nutrient cycling in that case do not have any influence on calculated TL and CL, the problem in translating non-exceedance according to TL or CL into site specific conditions is even larger since chemistry in that case is averaged both in time and space.

Calculated TL and CL-functions are dependent not only on the averaging method but also on whether averages are used for the future scenario only (method A), or for the historical input as well (method B and C). Recalibrating on base saturation typically has little effect on TL-functions and does not affect CL-functions at all since CL-functions are evaluations of steady-state chemistry. The effect that calibration on base saturation may have on TL-functions is due to the time-shift which a change in Gapon selectivity coefficients can cause. For the Söstarred site, however, the differences between the A, B and C methods were negligible for all but the TL 2030 function (Fig. 2).

As indicated in the introduction, it is an over-interpretation of the critical load concept to assume that a non-exceeded site never will experience violation of the chemical criteria used in calculating the critical load. This is due to the seasonal and rotational variations in soil chemistry. To illustrate this fact, six different deposition levels were chosen from TL2030 (Fig. 3) and used as the basis for a SAFE application at Söstarred using constant future deposition levels, but varying nutrient uptake and nutrient cycling. Even though the deposition levels used do not exceed the TL2030, the criteria still gets violated (Fig. 3) during certain parts of the rotation period.

That deposition levels given by the TL 2030 function leads to temporary violations of the criteria (Fig. 3) in a

simulation addressing rotational variations should not come as a surprise given the TL calculation method. If seasonal variations also were to be included additional temporary violations might appear. However, the primary aim with using TL functions and CL functions as basis for emission reduction negotiations is not to protect the chemistry of the soil per se, but rather the fauna and flora that are affected by soil chemistry. We deem it likely that whether or not “significant harmful effects” will appear is not only determined by the violation or absence of violation of the chosen criteria. We rather suspect that the link between criteria and effect involves how much the criteria is violated, over how long a time period, how frequently the violation events occur, in which part of the soil profile the criteria is violated, whether or not the violation events coincide with other stress factors, etc. In the current design of CL and TL calculations these issues cannot be addressed and our current knowledge is unfortunately limited.

With this in mind, it is high time to deepen the scientific discussion of the critical load concept from the never ending debate whether the used criteria is right or wrong, especially since many of the suggested chemical criteria, Bc/Al , total inorganic Al , pH and acid neutralizing capacity, all are interrelated: Just choosing another criteria will not automatically solve the problem as to how violation of the criteria and

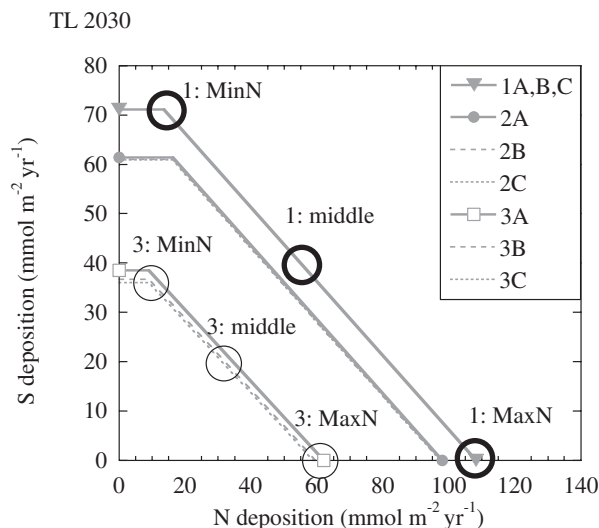
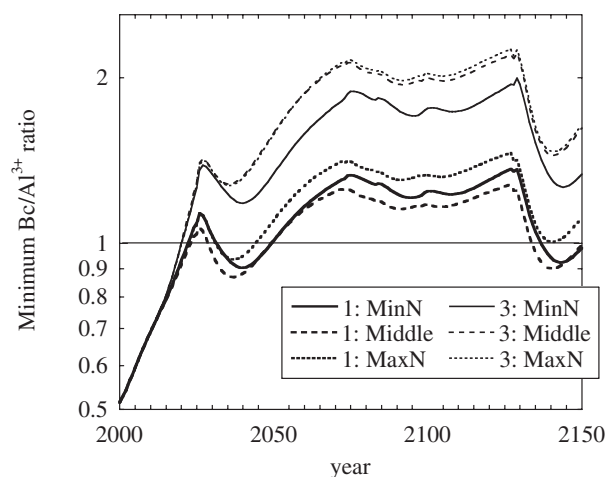


Fig. 3 The six chosen future deposition levels (*thick/thin circles*) and the corresponding minimum Bc/Al ratios (*thick/thin lines*) using varying nutrient uptake etc. It should be noted

Söstarred, dynamic simulations at TL 2030 deposition



that the relation between choice of position on the TL-function and shape of the dynamic result is site specific and dependent on e.g. the timing of thinning and other management events

effect on flora and fauna are related. We instead need to discuss and investigate what aspects of risk of damage the different criteria captures and what the time-delays between effects on chemistry and effects on biology are. Changing the criteria used in CL and TL calculations is a simple task, finding solid scientific support for such a change is much more difficult.

A decrease in acidifying deposition to TL2030 values will be beneficial for our forest ecosystems, simply because a decrease in acidifying deposition leads to a partial recovery from acidification. We do, however, conclude that it is far from certain that such a decrease will ensure full recovery at all sites. We therefore propose the calculation of *dynamic critical loads*, i.e. deposition levels at which the chosen chemical criteria is not violated during any part of the rotation period. If future research reveals softer limits for the used criteria, e.g. that short term violations can be accepted, the calculation method for dynamic critical loads could easily be adopted to accommodate that knowledge.

References

- Ågren, C. (2002). Reduction beyond expectations. *Acid News*, 2002(1), 18.
- Akselsson, C. (2005). Regional nutrient budgets in forest soils in a policy perspective, 2005. Doctoral Thesis, Department of Chemical Engineering, Lund University.
- Alveteg, M. (1998). Dynamics of forest soil chemistry. PhD dissertation. Lund University, Lund.
- Alveteg, M., Kurz, D., & Becker, R. (2002). Incorporating nutrient content elasticity in the MAKEDEP model. *Reports in Ecology and Environmental Engineering*, 1, 52–67.
- Bertills, U., Staaf, H., Akselson, C., Alveteg, M., Kronnäs, V., Moldan, F., et al. (2005). *Sweden*. In *CCE status report 2005 European critical loads and dynamic modelling*, CCE, ISBN no. 90-6960-128-1, pp. 142–171.
- Hettelingh, J. P., Posch, M., & Slootweg, J. (2005). *Status of European critical loads and dynamic modelling*. In *CCE status report 2005 European critical loads and dynamic modelling*, CCE, ISBN no. 90-6960-128-1, pp. 9–26.
- Hettelingh, J. P., Slootweg, J., & Posch, M. (Eds.) (2004). *Critical loads and dynamic modelling results*. CCE Status report 2004 259101014/2004, RIVM.
- Jenkins, A., Cosby, B. J., Ferrier, R. C., Larssen, T., & Posch, M. (2003). Assessing emission reduction targets with dynamic models: Deriving target load functions for use in integrated assessment. *Hydrology and Earth Science Systems*, 7(4), 609–617.
- Martinson, L., Alveteg, M., Kronnäs, V., Sverdrup, H., Westling, O., & Warfvinge, P. (2005). A regional perspective on present and future soil chemistry at 16 Swedish forest sites. *Water, Air and Soil Pollution*, 162, 89–105.
- Nilsson, J., & Grennfelt, P. (Eds.) (1988). Critical loads for sulphur and nitrogen. Report from a workshop held at Skokloster 19–24 March, Miljörapport 1988, 15. Stockholm: Nordic Council of Ministers.
- Posch, M., Hettelingh, J.-P., & Slootweg, J. (2003). *Manual for dynamic modelling of soil response to atmospheric deposition*. Technical Report 259101012/2003. The Netherlands: RIVM.
- Schöpp, W., Posch, M., Mylona, S., & Johansson, M. (2003). Long-term development of acid deposition (1880–2030) in sensitive freshwater regions in Europe. *Hydrology and Earth Science Systems*, 7, 436–446.
- Sverdrup, H., Martinson, L., Alveteg, M., Moldan, F., Kronnäs, V., & Munthe, J. (2005). Modeling recovery of Swedish ecosystems from acidification. *Ambio*, 34, 25–31.
- UNECE. (1999). Protocol to the 1979 convention on long-range transboundary air pollution to abate acidification, eutrophication and ground-level ozone. United Nations Economic Commission for Europe <http://www.unece.org/env/lrtap>.
- Wallman, P., Svensson, M. G. E., Sverdrup, H., & Belyazid, S. (2005). ForSAFE—An integrated process-oriented forest model for long-term sustainability assessments. *Forest Ecology and Management*, 207, 19–36.
- Warfvinge, P., Falkengren-Grerup, U., Sverdrup, H., & Andersen, B. (1993). Modelling long-term cation supply in acidified forest stands. *Environmental Pollution*, 80, 209–221.

Comparison of Critical Load Exceedance and Its Uncertainty Based on National and Site-specific Data

Liz Heywood · Richard Skeffington ·
Paul Whitehead · Brian Reynolds

Received: 17 June 2005 / Accepted: 2 February 2006 / Published online: 10 March 2007
© Springer Science + Business Media B.V. 2007

Abstract Critical loads have been used to develop international agreements on acidifying air pollution abatement, and within the UK and other countries, to develop national policies for pollution abatement. The Environment Agency (England and Wales) has regulatory obligations to protect sites of high conservation value from the threat of acidification, and hence requires a practical methodology for acidification assessments at the site-specific scale. The Environment Agency has therefore posed the question: Are the national critical load exceedance models sufficiently robust to form the basis for methods to assess harm to individual sites or are they only useful for national policy development? In order to provide one measure of the appropriateness of applying the models at the site-specific scale we incorporated estimates of uncertainty in both national and site-

specific data into the calculation of critical load exceedance for individual sites. The exceedance calculations use data from a wide range of sources and the accuracy of the exceedance will be influenced by the accuracy of the input data sets. Using Monte Carlo methods to incorporate the uncertainty in the input data sets into the calculation a distribution of critical load exceedance values is generated rather than a single point estimate. This paper compares uncertainty analyses for coniferous forested sites in England and Wales using both national scale and site-specific data sets and uncertainty ranges.

Keywords Acidification · Critical loads · Robustness · Uncertainty · Scale · Input data · Policy

L. Heywood (✉)
Centre for Ecology and Hydrology,
Monks Wood, Abbots Ripton,
Huntingdon, UK
e-mail: elhe@ceh.ac.uk

R. Skeffington · P. Whitehead
Aquatic Environments Research Centre,
Department of Geography, University of Reading,
P.O. Box 227, Reading, UK

B. Reynolds
Centre for Ecology and Hydrology,
Orton Building, Bangor, UK
e-mail: br@ceh.ac.uk

1 Introduction

Critical loads are being used to develop international agreements on acidifying air pollution abatement, and to formulate national strategies for pollution control. In England and Wales, they are being employed in the implementation of the EU Habitats Directive, which aims to protect a network of sites of national and international conservation importance. To determine whether a protected site is likely to be damaged by acidifying air pollutants, 1 km resolution critical loads extracted from the national critical load data sets for

acidity and nutrient nitrogen (Hall et al. 2003) are compared with deposition modelled by the FRAME long range transport model (Singles et al. 1998; Fournier et al. 2004). If the critical load is found to be exceeded, the sources contributing most to deposition may be required to reduce their emissions.

However, national scale data were designed for national and regional policy development and may not give accurate answers on individual sites because of scaling issues and the simplifying assumptions used in national models (Hall et al. 2007). Use of national critical loads and deposition data to calculate exceedances may thus lead to vulnerable sites being unprotected, or alternatively to unnecessary expenditure on emission control. This paper is an exploration of the extent to which using measured data available from research sites leads to different results from those achieved by using national data applied to the same sites. It uses uncertainty analysis to compare exceedance estimates from the two types of data.

2 Methods and Data

This study focused on three coniferous woodland sites across the UK; Liphook in the south east of England, Thetford in the east of England and Aber in Wales. These sites are not designated sites under the Habitats Directive, but were chosen because site-specific data were available. The Simple Mass Balance (SMB) model (Sverdrup and De Vries 1994) was used to calculate critical loads of acidity for coniferous woodland in the UK. Exceedance is defined simply as the difference between the deposition and critical load. When the deposition is greater than the critical load the exceedance is positive, and negative when it is lower than the critical load; a negative exceedance signifies no exceedance.

In this paper, we assumed that the uncertainty in exceedance could be calculated from an estimate of uncertainty in each of the parameters of the SMB and uncertainty in the deposition. This approach is sometimes referred to as a “parameter uncertainty analysis” (International Atomic Energy Agency (IAEA) 1989). It should be noted that uncertainties in model formulation and structure are not addressed by this type of analysis and hence an additional source of uncertainty is unaccounted for.

2.1 Specifying Input Parameters

Table 1 shows the site-specific values (SS) and national input values (N) and uncertainty ranges for terrestrial input parameters. Table 2 shows the default deposition parameters. For modelled deposition, earlier work by Abbott et al. (2002) suggested that a log-normal distribution giving a 95th percentile value equal to twice the mean was an appropriate estimate of uncertainty for oxidized N, and a log-normal distribution with a 95th percentile value of 1.5 times the mean for the other deposition parameters. The choice of default values, ranges, distributions and correlations is critical for this analysis. Derivation of the national default values can be found in Hall et al. (2003) and the sources of the ranges and distributions in Heywood et al. (2006). It is important to take account of correlation between parameters as they may have a large effect on the results of the uncertainty analysis. Correlations were estimated between parameters where there were either sufficient data to explicitly calculate them or where there were strong theoretical reasons for the correlations. Derivation of the site-specific default values, uncertainty ranges and correlations can be found in Skeffington et al. (2006a).

The different choice of distribution type for national and site-specific is an outcome of the different ways the uncertainty ranges were derived. As a precautionary measure, rectangular distributions were used for site-specific data because there was no good evidence that a central value was more likely. In fact, only weathering in the site-specific data was really a measured value, as the others are all long-term sustainable estimates, defaults dependent on soil type or estimated rather indirectly (runoff). National data represent average conditions over a large number of sites, and hence it was thought appropriate to use normal distribution for some national parameters.

2.2 Uncertainty Propagation

Monte Carlo methods (Rubenstein 1981) were used to propagate the uncertainty in all the input parameters to the exceedance calculation (inputs to the SMB and acidifying deposition). A random value is sampled from the distribution specified for each uncertain model parameter, and a single estimate of critical load exceedance, is calculated. This process

Table 1 Default values and uncertainty ranges for Liphook, Thetford and Aber sites where N denotes national data, SS site-specific data and SD standard deviation

Parameter	Site/Scale	Input	Lower	Upper	SD	Distribution
Base cation weathering ($\text{eq.ha}^{-1}\text{yr}^{-1}$)	Liphook N	100	0	200		Rectangular
	Liphook SS	150	50	250		Rectangular
	Thetford N	4,000	2,000	6,000		Rectangular
	Thetford SS	4,600	2,300	6,900		Rectangular
	Aber N	350	200	500		Rectangular
	Aber SS	163	120	300		Rectangular
Base cation uptake ($\text{eq.ha}^{-1}\text{yr}^{-1}$)	Liphook N	270			62	Normal
	Liphook SS	270	135	540		Rectangular
	Thetford N	270			62	Normal
	Thetford SS	270	135	540		Rectangular
	Aber N	270			62	Normal
	Aber SS	316	284	348		Rectangular
Calcium correction factor (dimensionless)	Liphook N	0.1	0	0.2		Rectangular
	Liphook SS	0.57	0.47	0.67		Rectangular
	Thetford N	1	0.8	1		Rectangular
	Thetford SS	0.9	0.85	0.95		Rectangular
	Aber N	0.1	0	0.2		Rectangular
	Aber SS	0.092	0.042	0.142		Rectangular
Calcium uptake ($\text{eq.ha}^{-1}\text{yr}^{-1}$)	Liphook N	160			43.2	Normal
	Liphook SS	125	80	320		Rectangular
	Thetford N	160			43	Normal
	Thetford SS	160	80	320		Rectangular
	Aber N	160			43	Normal
	Aber SS	160	80	320		Rectangular
Runoff ($\text{m}^3.\text{ha}^{-1}\text{yr}^{-1}$)	Liphook N	4100			943	Normal
	Liphook SS	4,690	4,221	5,159		Rectangular
	Thetford N	1,620			373	Normal
	Thetford SS	1,620	1,458	1,782		Rectangular
	Aber N	13,800			3,174	Normal
	Aber SS	5,930	5,337	6,523		Rectangular
Ca/Al _{crit} (mol.mol^{-1})	All sites	1	0.5	1.5		Rectangular
Gibbsite coefficient (m^6eq^{-2})	Liphook N	950	760	1140		Rectangular
	Liphook SS	950	300	3,000		Rectangular
	Thetford N	950	760	1140		Rectangular
	Thetford SS	950	300	3,000		Rectangular
	Aber N	100	80	120		Rectangular
	Aber SS	100	10	380		Rectangular
Nitrogen immobilisation ($\text{eq.ha}^{-1}\text{yr}^{-1}$)	Liphook N	214	107	321		Rectangular
	Liphook SS	214	107	321		Rectangular
	Thetford N	71	35.5	107		Rectangular
	Thetford SS	71	35.5	107		Rectangular
	Aber N	214	107	321		Rectangular
	Aber SS	150	120	180		Rectangular
Nitrogen uptake ($\text{eq.ha}^{-1}\text{yr}^{-1}$)	Liphook N	210			57	Normal
	Liphook SS	500	400	600		Rectangular
	Thetford N	210			57	Normal
	Thetford SS	210	105	420		Rectangular
	Aber N	210			57	Normal
	Aber SS	246	221	271		Rectangular
Denitrification ($\text{eq.ha}^{-1}\text{yr}^{-1}$)	Liphook N	71	36	107		Rectangular
	Liphook SS	71	35.5	107		Rectangular

Table 1 (continued)

Parameter	Site/Scale	Input	Lower	Upper	SD	Distribution
	Thetford N	71	36	107		Rectangular
	Thetford SS	71	35.5	107		Rectangular
	Aber N	71	35.5	107		Rectangular
	Aber SS	35.5	28	43		Rectangular

N is national data and SS is site specific data

was repeated 5,000 times to produce a stable output and provide a probability distribution of exceedance.

The probability distributions are expressed in this paper as statistical measures. The mean and median values are given as estimates of the values around which the distribution is clustered. The 5th and 95th percentiles and standard deviation are given as measures of the dispersion. The probability of exceedance is calculated from the probability distribution as the likelihood that the site will be exceeded. The deterministic result is the value calculated using the default input parameters with no uncertainty incorporated.

3 Results and Discussion

3.1 Input Data

The input values differ depending on whether national or site-specific data are used. High quality measurements are often available for individual sites whilst at the national scale input data usually have to be derived from other sources, such as regional soil maps, statistics from experimental datasets or expert judgement. For example, national estimates of soil mineral weathering rate are based on the Skokloster classification (Nilsson and Grennfelt 1988) using national soils databases, whereas site-specific values may be derived from geochemical measurements or modelling techniques applied to the soil present at the site (e.g. Langan et al. 1996). In addition, national critical load calculations use single default values for nitrogen and base cation uptake by coniferous plantation forestry. The values are derived from measurements at a number of sites across the country and the mean value applied to all coniferous forestry, irrespective of tree species. For individual sites, information from harvested trees can be used (e.g. Reynolds et al. 1998) to give a more accurate estimate

of nutrient removal. Local knowledge of soil may be used to give appropriate ranges for the gibbsite equilibrium constant at the site level, compared to national estimates that use default values based on generalized soil characteristics.

Liphook and Aber both have a large amount of site-specific data (Tables 1 and 2). The site-specific and national input parameters differ significantly for Liphook but less so for Aber. The input parameters for the Thetford site differ only for weathering rate and calcium correction factor. The effects these differences have on exceedance are discussed in Section 3.2.

It would be expected that the uncertainty ranges for the input parameters for the site-specific analysis should be narrower than those for the national analysis as we may have better knowledge based on detailed site measurements in space and time. Table 1 does show that in general site-specific uncertainty ranges are narrower. For a few variables the site-specific uncertainty range is wider than the national one. For instance the national uncertainty range for base cation weathering at Thetford does not encompass the maximum estimate for the site-specific value. To some extent this is an artifact of the way the uncertainty ranges have been defined: both the

Table 2 Default deposition parameters for Liphook, Thetford and Aber where N denotes national data, SS site-specific data

Site/Scale	NH ₄ _{dep}	NO ₃ _{dep}	^a S _{dep}	^a BC _{dep}	Ca _{dep}
Liphook N	1350	1190	780	300	430
Liphook SS	513	392	653	582	175
Thetford N	1,640	1,240	490	190	220
Thetford SS	1,640	1,240	490	190	220
Aber N	1,190	940	830	180	310
Aber SS	1,190	940	1,481	397	485

Values are in eq.ha⁻¹ yr⁻¹. ^a denotes non-marine deposition. The national deposition value is the average for the 5 km grid square which contains the site.

national and site-specific estimates are based on an uncertainty range of $\pm 50\%$ but the nominal site-specific input value is larger hence the maximum value is larger also. This occurs for a number of variables although the national uncertainty ranges always encompasses the site-specific input value.

3.2 Deterministic Results

Table 3 shows the deterministic results of critical load exceedance using national and site specific input data. For Liphook there is a difference of $2,100 \text{ eq ha}^{-1} \text{ yr}^{-1}$ between predictions because the estimated site-specific deposition for the nitrogen species is only 30% of the national estimate in that grid cell. For Thetford, there is very little site-specific data, and the exceedance differs by $738 \text{ eq ha}^{-1} \text{ yr}^{-1}$ because of a small difference in weathering rate. For Aber, the site-specific estimate of S deposition is 78% higher than the national estimate, runoff is 57% less and weathering is 53% less (Tables 1 and 2). Exceedance is therefore greater by $400 \text{ eq ha}^{-1} \text{ yr}^{-1}$ using the site-specific parameters.

The deterministic results for the Liphook site show that different conclusions would be reached about critical load exceedance depending on whether national or site-specific data are used. The national data predict that the site is highly exceeded and the site-specific data predict no exceedance. The Aber analyses also gave quite different deterministic results, although both predicted the site was exceeded regardless of whether site-specific or national data were being used. The results of the Thetford analyses showed good agreement predicting that the site was

not exceeded irrespective of the type of data used because these data sets differ only in weathering rate.

3.3 Monte Carlo Analysis

Table 3 also shows the means, standard deviations, and 5th, 50th and 95th percentiles of the exceedance distributions. For Liphook, the mean for the site-specific analysis ($210 \text{ eq ha}^{-1} \text{ yr}^{-1}$) lies outside the 90% confidence intervals for the national analysis, indicating that the analyses predict very different results. Some of the differences between national and site-specific data may be due to spatial variation e.g. the national deposition data are supplied as average deposition over a 5 km grid square, whereas measured deposition is for a single point. Though spatial variation is not strictly uncertainty, knowledge of its magnitude is uncertain and it can be treated in similar ways (Skeffington et al. 2006b). For Thetford and Aber the mean values for the site-specific analysis (-8408 and $1295 \text{ eq ha}^{-1} \text{ yr}^{-1}$, respectively) are in good agreement with the national analysis (-7089 and $1052 \text{ eq ha}^{-1} \text{ yr}^{-1}$, respectively) and both sets of analyses lie well within one standard deviation of each other. The site-specific analysis for Thetford predicts a slightly higher uncertainty than the national analysis which is probably due to the higher weathering rate used in the site-specific analysis. The means of the Monte Carlo analysis agree with the deterministic results; for Thetford both predict non-exceedance and for Aber exceedance. The Liphook deterministic site-specific result however predicts non-exceedance whilst the mean of the Monte Carlo analysis suggests that the site is exceeded.

Table 3 Predicted values for the deterministic and uncertainty analysis of critical load exceedance for Liphook, Thetford and Aber where N denotes national data, SS site-specific data

Simulation	Deterministic	Uncertainty analysis					
	Value	Mean	Standard deviation	Probability of exceedance (%)	5th %ile	50th %ile (Median)	95th %ile
Liphook N	2,095	2,177	811	100	1,009	2,106	3,597
Liphook SS	-15	210	459	68	-558	217	949
Thetford N	-7,323	-7,089	3,656	0.3	-14,019	-6,748	-1,913
Thetford SS	-8,061	-8,408	4,138	2	-16,210	-8,023	-2,662
Aber N	935	1052	748	93	-105	1,006	2,354
Aber SS	1,335	1,295	618	96	213	1,396	2,237

Values are in $\text{eq ha}^{-1} \text{ yr}^{-1}$.

The probability distributions of the predicted exceedance at each site were used to calculate the probability that the rate of deposition was lower than the critical load (Probability of Exceedance statistics in Table 3). The results of the site specific and national analyses were very different for the Liphook site where the national analysis predicted a 100% probability of exceedance, i.e. certain risk of acidification. However the site specific analysis predicts only a 68% probability that the site is exceeded, indicating less confidence in the exceedance prediction. The national analysis for Aber showed a high level of confidence that the site is exceeded and the site-specific study also predicted a very high level of confidence. For Thetford, the probability of exceedance is less than 5% for both sets of analyses suggesting with a high degree of confidence that the critical load is not exceeded at this site.

At Liphook the 5th percentile of the national exceedance distribution is greater than zero, suggesting it is likely that the site is exceeded. The site-specific study shows the 5th percentile is below zero (and the 50th percentile above zero), indicating greater uncertainty about exceedance. If a highly precautionary approach based on whether the 95th percentile of the distribution is greater than zero is adopted both analyses conclude that the site is exceeded. For Aber the national analysis predicts a 50th percentile value above zero and a 5th percentile below zero so that a policy maker may once again opt to consider that the critical load is exceeded or that further study is required. However the site-specific analysis the 5th percentile is above zero indicating that the site is exceeded. For Thetford the 95th percentile values are below zero for both analyses, indicating that it is likely that the site is not exceeded.

At Liphook the 95th percentile of the site-specific analysis ($949 \text{ eq. ha}^{-1} \text{ yr}^{-1}$) is smaller than the 5th percentile of the national analysis ($1009 \text{ eq. ha}^{-1} \text{ yr}^{-1}$) so the two distributions hardly overlap with the national analysis predicted significantly higher exceedance than the site-specific analysis. This demonstrates how the differences in the input data manifest themselves in the variability of the exceedance predictions. For Thetford and Aber the 5th, 50th and 95th percentiles are similar for both distributions indicating that there is a significant overlap between probability distributions, although for Thetford the national data predict higher exceedances whereas for

Aber it is the site-specific data which does so. The distributions for Thetford show that even a site with a large deterministic negative exceedance, there can be a small tail of exceeded values. No general relationship between national and site-specific critical load exceedance uncertainty probability distributions can be established from the analysis of these three sites.

4 Concluding Remarks

These example sites in this paper illustrate how the application of national data at a site scale should be treated with care and highlights:

- Input default values and uncertainty ranges for a research site may be different to data derived for national purposes.
- The exceedance probability distributions based on site specific and national data can vary significantly from one site to another. Liphook varied significantly although Aber gave good agreement. Thetford also gave good agreement although more estimates of site specific data are required to make better judgements for this site.
- The user needs to be aware of the potential for error in both approaches, especially where national data have to be used because the site specific data do not exist or are too costly to collect.
- This paper provides some information on how to deal with the conflict between data availability and uncertainty. However the current data set is too limited to draw final conclusions on this topic. More site-specific data should be collected in order to achieve this.

Acknowledgements The authors gratefully acknowledge the Environment Agency (E&W) for their contribution to the funding of this research. However, the views expressed are those of the authors.

References

- Abbott, J., Hayman, G., Vincent, K., Metcalfe, S., Dore, T., Skeffington R., et al. (2002). Uncertainty in acid deposition modelling and critical load assessments, *R&D Technical Report P4-083(5)/1*, AEA Technology plc, Culham Science Centre, Abingdon, Oxfordshire, OX13 3ED.
- Fournier, N., Dore, A. J., Vieno, M., Weston, K. J., Dragosits, U., & Sutton, M. A. (2004). Modelling the deposition of

- atmospheric oxidised nitrogen and sulphur to the United Kingdom using a multi-layer long-range transport model. *Atmospheric Environment*, 38(5), 683–694.
- Hall, J., Ulllyett, J., Heywood, L., Broughton, R., Fawehinmi, J., & 31 UK experts (2003). Status of UK Critical Loads: Critical Loads Methods, Data and Maps, *Report to Defra*, CEH Monks Wood, Abbots Ripton, Huntingdon, PE28 2LS. <http://critloads.ceh.ac.uk>.
- Hall, J., Ulllyett, J., Wadsworth, R., & Reynolds, B. (2007). The applicability of national critical loads data in assessing designated sites. *Water, Air, and Soil Pollution Focus*, doi:10.1007/s11267-006-9091-9.
- Heywood, E., Hall, J., & Reynolds, B. (2006). A review of uncertainties in the inputs to critical loads of acidity and nutrient nitrogen for woodland habitats. *Environmental Science and Policy*, 9, 78–88.
- International Atomic Energy Agency (IAEA) (1989). Evaluating the reliability of predictions made using environmental transfer models. In *IAEA Safety Series 100*, Vienna, Austria.
- Langan, S. J., Reynolds, B., & Bain, D. C. (1996). The calculation of base cation release from mineral weathering in soils derived from palaeozoic greywackes and shales in upland UK. *Geoderma*, 69, 275–285.
- Nilsson, J., & Grennfelt, P. (1988). Critical Loads for Sulphur and Nitrogen, NORD 1998:97, Nordic Council of Ministers, Copenhagen, Denmark, pp. 418.
- Reynolds, B., Wislon, E. J., & Emmett, B. A. (1998). Evaluating critical loads of nutrient nitrogen and acidity for terrestrial systems using ecosystem-scale experiments (NITREX). *Forest Ecology and Management*, 101, 81–94.
- Rubenstein, R. Y. (1981). *Simulation and the Monte Carlo method*. New York, NY: Wiley.
- Singles, R., Sutton, M. A., & Weston, K. J. (1998). A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. *Atmospheric Environment*, 32, 393–399.
- Skeffington, R., Hall, J., Heywood, L., Wadsworth, R., Whitehead, P., Reynolds, B. et al. (2006a). *Estimating uncertainty in critical load assessment models*. [Acidification and annual audits], Final report to the Environment Agency, R&D Project P4-120/4, CEH Monks Wood.
- Skeffington, R. A., Whitehead, P. J., & Abbott, J. (2006b). Quantifying uncertainty in critical loads: (B) acidity mass balance critical loads on a sensitive site. *Water, Air, and Soil Pollution*, 169, 25–46.
- Sverdrup, H., & De Vries, W. (1994). Calculating critical loads with the simple mass balance method. *Water, Air, and Soil Pollution*, 72, 143–162.

Setting Site Specific Critical Loads: An Approach using Endorsement Theory and Dempster–Shafer

Richard A. Wadsworth · Jane R. Hall

Received: 17 June 2005 / Revised: 17 February 2006 / Accepted: 3 December 2006 / Published online: 23 January 2007
© Springer Science + Business Media B.V. 2007

Abstract There is an increasing demand from conservation agencies for site-specific critical loads (CL); unfortunately, there is often very little specific information on a site to determine the important parameters needed to calculate the CL or on the spatial location of the “designated feature” in a site. Determining the most appropriate CL therefore involves using expert judgement to make decisions with incomplete and uncertain information. Endorsement Theory (Cohen, 1985) and Dempster–Shafer statistics (Dempster, 1967; Shafer, 1976) are, respectively, a decision-theoretic and a statistical technique for reasoning under those conditions (uncertainty and incompleteness). A key reason for applying these techniques is that they make expert opinion explicit and available for scrutiny. Both techniques have been applied to the problem of setting an appropriate site specific CL, using heathland sites as a case study. Initial findings are encouraging; the uncertainty in expert judgement is made explicit, the end results are intuitively reasonable and the methodology apparently acceptable to decision makers.

Keywords Endorsement Theory · Dempster–Shafer · uncertainty · site specific critical loads

1 Introduction

A Critical Load (CL) is “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.” The concept arose in the 1980s as a response to concerns over transboundary (international) air pollution and particularly “acid rain.” Because of these concerns a tool or methodology was required to help in assessing the effect of alternative policy options to control the emission of pollutants, and their subsequent dispersal, deposition and impact; CL were therefore designed to work at the broad level of international agreements and protocols (see <http://critloads.ceh.ac.uk> for more details). They are most commonly calculated for acidity (caused by sulphur and nitrogen oxides) and eutrophication (nitrogen); CL are calculated for soils and freshwaters. Over the last two decades a number of refinements to the methodology and data have been made, however, across all of Europe there are only a handful of locations where all the information required to calculate the soil acidity CL has been measured. Recently there has been an increasing demand from conservation agencies for site-specific CL, particularly for sites designated for biological conservation (Special Areas of Conservation, Special Protection Areas, etc.). Using national data to generate site specific values can give misleading results; generally the location of the boundaries of

R. A. Wadsworth (✉) · J. R. Hall
CEH Monks Wood,
Abbots Ripton, Huntingdon,
Cambridgeshire PE28 2LS, UK
e-mail: rawad@ceh.ac.uk

the site are unavailable and the site is reduced to a “point”, national data use of the dominant soil and land cover in a 1 km² and these may be wrong or inappropriate for the site. In a national estimate with many hundreds of sites these errors will cancel each other out and a robust estimate can be made (of the national situation), but for someone familiar with a particular site any discrepancies will be disconcerting.

There is usually only a limited amount of relevant site-specific information and what information that is available often requires interpretation. One piece of information that is always available from the Conservation Agencies is the vegetation type, which is always described within well-defined and detailed classification systems. We sought an analysis method that would allow us to exploit whatever local information was available whilst making the uncertainty in expert opinion an explicit part of the reasoning process; Endorsement Theory (Cohen, 1985) which was designed for reasoning with incomplete information meets these requirements. Confidence in the CL estimated from the site-specific information will be variable; the “best” CL value should combine both the local and national estimates. We wished to keep the uncertainty in both estimates explicit and therefore combine both strands of evidence using Dempster–Shafer (Dempster, 1967; Shafer, 1976) which in this context is effectively an extension of Bayesian statistics.

2 Using Endorsement Theory to Set Site Specific Critical Loads

Endorsement Theory (ET) (Cohen, 1985) is a form of reasoning with incomplete and uncertain evidence. The approach was developed in the AI (artificial intelligence) community in an attempt to develop systems that could reason in a more human manner and particularly the ability of human experts to “diagnose” situations with limited information. The approach is particularly useful for:

- Allowing inference to be made from partial knowledge.
- Making the reasoning process explicit, traceable and highly heuristic.
- Avoiding the need to translate expert knowledge into numerical values.

In the case of trying to set a site specific CL we typically do not have much information on the environmental conditions in the designated site, even such crucial information as the soil series is not consistently readily available. Typically the location of the designated feature (i.e., habitat or species) is unknown (or is unavailable), nor is there often information on the relationship between the designated feature and the limited number of habitats for which CL methods are available. ET is a way of marshalling whatever local information we may be able to obtain for a site and of providing a very simple indication of the expected reliability of the information.

In the UK soils have been categorised into six acidity CL classes; five for mineral and organo-mineral soils (Hornung et al., 1995; Loveland, 1991), and a sixth class for the peat soils for which a different methodology is used (Calver, Cresser, & Smart, 2004). For the purpose of using ET we consider each CL class *as if* it were a separate hypothesis. We seek to determine the extent to which the available data supports each hypothesis. The procedure to produce an endorsement for a CL for a site can be summarised as;

- Determine what “designated features” exist on the site; these can be habitats or species and in general information on their exact location is unavailable.
- Assume that protecting the existing vegetation will protect the designated feature.
- Reclassify the recorded vegetation classes in terms of the National Vegetation Classification (NVC) (Rodwell, 1991 et seq) (many sites are already described in terms of the NVC).
- Using the descriptions in the Rodwell books obtain information about the environment where the relevant NVC class(es) is typically found.
- Process the environmental information in Loveland (ibid) to produce Look-up-Tables of the “weight of evidence” than an environmental factor gives to each CL class.
- Link the environmental information from the NVC to the environmental information in Loveland (ibid) on the basis of common terms and synonyms.
- Combine the “weights of evidence” for all the environmental factors relating to an NVC class to produce an “endorsement” for each CL class.

2.1 Primary Information Sources

Information on the designated features and the vegetation cover of the designated sites is always obtainable from the Conservation Agencies and will not be discussed further.

The NVC (Rodwell, 1991 et seq) is the de-facto standard description of natural and semi-natural vegetation communities in the UK. Each class is described over several (~10) pages of text, but, the amount of environmental information (soils, geology, topography, climate, geography, management etc.) is inconsistent; communities are also very variable in their fidelity to particular conditions. Information about each class has been extracted and stored in an MS Access database as text using Rodwell's vocabulary; examples for two heath communities are shown in Table 1.

Loveland (ibid) uses the methodology documented in Hornung et al. (1995) to allocate 298 soil associations in England and Wales into one of the six CL acidity classes. Information on the physical characteristics of the *dominant* soil series in each association is also provided, for example, for the Worcester association (431):

Geology	Permo-Trias red mudstone
Mineralogy	Chlorite/carbonates
Texture	Clayey/fine loam
Land Use	Stock rearing/arable
Comment	Slow drainage.
CL class	2.0–4.0 keq ha ⁻¹ yr ⁻¹

All soil associations are described in the national hierarchical soil classification scheme (NSRI, Soil Survey, 1983); the Worcester association (431) being:

Major group	Pelosols
Sub-group	Argillic pelosols
Type	Typical argillic pelosol

The data in Loveland has been summarised into seven look-up-tables (LUT); “soil association,” “major group,” “sub-group,” “type,” “texture,” “geology” and “comment,” (that is excluding “mineralogy” and “land use”). In each LUT the cells in the table record the number of soil associations that share a particular attribute and have been allocated to a particular CL class. In Table 2 (an example LUT) it can be seen that there are a total of 130 soil associations in the major

Table 1 Examples of environmental information abstracted from Rodwell (1991)

	H1 <i>Calluna vulgaris</i> – <i>Festuca ovina</i> heath	H21 <i>Calluna vulgaris</i> – <i>Vaccinium myrtillus</i> – <i>Sphagnum capillifolium</i> heath
Soil series	Newport + Worlington	
Soil type	Brown sands + Non-calcareous brown sands	Fragmentary humic rankers
Soil texture	Sandy + Sandy-skeletal	
Geology	Sandy glacio-fluvial drift + Arenaceous + Aeolian sand	
Soil pH	Acid + Low surface pH	
Soil nutrient status	Oligotrophic + Impoverished	
Soil processes	Signs of podzolisation	
Geological processes	Periglacial sorting + Decalcification	
Hydrology	Free to excessively drained	Free draining but always moist
Topography	Lowland + 30 m (1 to 76 m)	Steep sunless slopes + 289 m (15 to 640 m) + 34 degrees (3 to 90 degrees)
Management	Burning and grazing	Very sensitive to burning

Table 2 Count of soil associations by major soil group and critical load class

Major group	Critical Load Class (ranges in $\text{keq ha}^{-1} \text{ year}^{-1}$)						Total
	0.0–0.2	0.2–0.5	0.5–1.0	1.0–2.0	2.0–40	peat	
Brown soil	3	27	57	3	40		130
Ground-water gley	6	4	7	9	16		42
Lithomorphie	1	4			20 (s)		25
Man-made						5	5
Peat						11 (s)	11
Pelosols		1	1		5		7
Podzol	20	9					29
Raw gley			1				1
Surface-water gley		6	9	30	3		48

(s) Groups that provide a strong endorsement for a CL class.

group “brown soils,” of which three have a CL of 0–0.2 $\text{keq ha}^{-1} \text{ year}^{-1}$; 27 have a CL of 0.2–0.5 $\text{keq ha}^{-1} \text{ year}^{-1}$; 57 a CL of 0.5–1.0 $\text{keq ha}^{-1} \text{ year}^{-1}$ and so on.

Table 2 shows that some “major groups” have a high fidelity to a particular CL class e.g. “podzol,” others eg “brown soils” are much more variable and the “lithomorphie” group appears to be bi-modal (those derived from chalk and limestone versus those derived from granite and sandstone).

Expert opinion is used to decide how much “weight of evidence” should be put on each entry in the LUT; for example how much reliance should be put on the observation that 3 out of 130 soil associations in the “brown soil” group have a low CL and how much weight should be given to the observation that 20 out of 29 “podzol” group have a high CL? We contend that most people consider that 20 out of 29 provides stronger evidence than 3 out of 130; the question is how to express that belief? In a standard knowledge engineering approach numerical scales are used eg choose a number between 0 and 10. In ET the scale is expressed in words (e.g. weak, strong, overwhelming) and it is the responsibility of the domain expert and not the knowledge engineer to define this “scale.” We used a scale with four categories; “strong,” “moderate,” “weak” and “very weak.” Other experts may prefer other categories; in the context of land cover change Comber, Law, and Lishman (2003) use; “conclusive,” “prima-facie,” “strong” and “weak”; whatever scale is chosen by the domain expert they have to be explicit. Having

defined their scale the expert needs to allocate each value in the LUT into one of their categories. In this case the two cells marked “s” in Table 2 are the only ones to provide a “strong” weight.

2.2 Relating NVC Soils Information to Soils Terminology used by Loveland

The environmental information provided about each NVC classes needs to be related to the terminology used by Loveland. Sometimes there is an exact correspondence between terms used in the NVC and in Loveland and the NSRI. More often terms are similar but different, for example, “brown soil” in Loveland and “brown earth” in the NVC. In some cases there is no correspondence; for example, several NVC communities are associated with the “Borrowdale Volcanics” in the Lake District, but Loveland does not use that term. A LUT is used to relate the NVC terms to the Loveland terms, in linking the terms we are conservative and when in doubt we do not infer a connection.

2.3 Combining the Evidence to Produce an Endorsement

The weights of evidence for each piece of environmental information are collated and combined to produce an overall endorsement for each CL class for the NVC class in question; in ET the categories are determined by the domain expert and are

expressed in words not numbers. We use a scale with five levels of endorsement:

- “Definitive,” three pieces of “strong” evidence and no conflicting evidence.
- “Confident,” two pieces of “strong” evidence and no “strong” conflict.
- “Likely,” at least one piece of “strong” evidence or three “moderates.”
- “Possible,” at least one “moderate” or two “weak” pieces of evidence.
- “Weak,” at least one piece of evidence.

Table 1 shows the environmental data for two NVC heathland classes: H1 (*Calluna vulgaris* – *Festuca ovina*) and H21 (*Calluna vulgaris* – *Vaccinium myrtillus* – *Sphagnum capillifolium*). There are multiple entries for some attributes (for example H1 has three references to geology) and each of these “statements” is treated independently and given equal weight. Table 3 provides all the evidence for H1 that could be extracted.

In this case we cannot give a “definitive” endorsement but we are “Confident” that the H1 heath should have a CL class 0.2–0.5 keq ha⁻¹yr⁻¹. It is “Likely” that the CL is lower but there are only “weak” or “possible” endorsements for a higher CL. Repeating the process with H21 reveals a problem; H21 is associated with “fragmentary humic ranker” soils which are in the lithomorph group. Most (20 out of 25) lithomorph soils (the rendzinas) have a high CL (as they are derived from chalk or limestone). This leads to a strong endorsement for a high CL for

H21, whereas a lower CL is more appropriate for humic ranker soils.

Of the 22 NVC Heaths none were awarded a “definitive” endorsement and only five had a “confident” attribution. Twelve Heaths are associated with rankers (lithomorph soils) and therefore like H21 have erroneous “Likely” endorsements for a high CL. If a strict interpretation of the “precautionary principle” were adopted (i.e., any evidence no matter how weak) all but two of the Heaths would be allocated to the lowest CL class.

3 Combining National and Local Estimates

ET provides an estimate of the CL for a site based on knowledge about the NVC classes; however, the CL can also be estimated from the national-scale data (<http://critloads.ceh.ac.uk>) based on the dominant soil in each 1 km grid square. In combining the local (ET approach) and the national data we assume:

- Both strands of evidence are uncertain.
- Both strands of evidence have value.

To combine both estimates we need to either convert the national estimates into words to be compatible with ET or convert the endorsements from words to numbers, we choose the latter. Bayesian inference is concerned with the extent to which our belief in a hypothesis increases or decreases as a new piece of evidence becomes available. Dempster–Shafer (DS) (Dempster, 1967; Shafer, 1976) can be

Table 3 Endorsement summary for H1 *Calluna vulgaris* – *Festuca ovina* Heath

LUT	Loveland Term	NVC Term (Table 1)	Critical Load Class (ranges in keq ha ⁻¹ year ⁻¹) ^a				
			0.0–0.2	0.2–0.5	0.5–1.0	1.0–2.0	2.0–4.0
Soil name	Newport	Newport		Strong			
	Worlington	Worlington		Strong			
Soil group	Brown soil	Brown sands	V. weak	Weak	Weak	V. weak	Weak
	Brown soil	Non-calcareous brown sands	V. weak	Weak	Weak	V. weak	Weak
Soil Texture	Sand	Sandy	Mod'	Weak			V. weak
	Sand	Sandy-skeletal	Mod'	Weak			V. weak
Geology	Drift (with sandstone peat)	Sandy glacio-fluvial drift	Weak	Weak	V. weak		V. weak
	Sand/sandstone	Arenaceous	Mod'	Weak		V. weak	
	Sand/sandstone	Aeolian sand	Mod'	Weak		V. weak	
Overall Endorsements			Likely	Confident	Possible	Weak	Possible

^a No evidence for the “peat” hypothesis which is omitted from this table.

Table 4 Conversion of endorsement to numerical values of belief, uncertainty and disbelief

Endorsement	Belief	Uncertainty	Disbelief
“Definitive”	0.90	0.1	0.00
“Confident”	0.75	0.2	0.05
“Likely”	0.50	0.3	0.20
“Possible”	0.25	0.3	0.45
“Weak”	0.10	0.4	0.50

considered an extension of the Bayesian approach which is useful because:

- it provides an explicit representation of uncertainty and,
- weak evidence for something does not imply strong evidence for the opposite.

In DS belief and plausibility provide the upper and lower bounds of probability for a proposition; belief+uncertainty=plausibility and belief+uncertainty+disbelief=1.

3.1 Estimating Uncertainty

Hall, Ulyett, Heywood, Broughton, and Fawehinmi (2004) investigated the uncertainty in national estimates using a Monte Carlo approach. They generated a mean CL and variance for every 1 km² based on the dominant and sub-dominant soils; and showed that the assumption of a Gaussian distribution was reasonable. Given a mean and standard deviation the probability (belief) that the true value is within any particular range can be easily calculated from the cumulative probabilities of the class limits, (e.g. using “normdist” in Microsoft Excel). Converting the ET endorsements into numerical values is a classic knowledge engineering problem and the values in Table 4 express our expert opinion, the key method-

ological issue is that they are explicit, and therefore open to scrutiny and investigation into how sensitive the results are to the values selected.

3.2 Mathematical Formulation

To combine two strands of evidence we use the form of DS suggested by Tangestani and Moore (2002):

$$B_{12} = (B_1 * B_2 + B_1 * U_2 + B_2 * U_1) / \beta \quad (1)$$

$$\beta = 1 - B_1 * D_2 - B_2 * D_1 \quad (2)$$

Where:

B = belief, D = disbelief & U = uncertainty;
 β is a normalising factor, (to ensure that $B+D+U=1$).

3.3 A Worked Example

Consider a site covered in H1 heath where the national data estimate a mean CL of 0.6 keq ha⁻¹ year⁻¹, a standard deviation of 0.2 and a Gaussian distribution. Table 5 summarises the beliefs from the ET (local) and national estimates.

The strongest endorsement is for the CL class 0.2–0.5 keq ha⁻¹ year⁻¹. From Table 5; $B_1=0.75$, $U_1=0.2$,

Table 5 Summary for the worked example

CL Class ^a	Endorsement (Table 3)	Endorsement as numbers (Table 4)			National (with $\mu=0.6$, $\sigma=0.2$, Gaussian distribution)		
		Bel ₁	Unc ₁	Dis ₁	Bel ₂	Unc ₂	Dis ₂
0.0–0.2	Likely	0.50	0.3	0.20	0.021	0.0	0.979
0.2–0.5	Confident	0.75	0.2	0.05	0.286	0.0	0.714
0.5–1.0	Possible	0.25	0.3	0.45	0.669	0.0	0.331
1.0–2.0	Weak	0.1	0.4	0.50	0.023	0.0	0.977
2.0–4.0	Possible	0.25	0.3	0.45	0.0	0.0	1.0

^a Class ranges in keq ha⁻¹ year⁻¹.

$D_1=0.05$ & $B_2=0.286$, $U_2=0.0$, $D_2=0.714$. Applying the equations:

$$\beta = (1 - 0.75 * 0.714 - 0.286 * 0.05) = 0.450$$

$$B_{12} = (0.75 * 0.286 + 0.75 * 0.0 + 0.286 * 0.2) /$$

$$0.450 = \underline{\underline{0.604}}$$

In contrast the national data give the highest probability to the hypothesis of CL class 0.5–1.0 keq ha⁻¹ year⁻¹; from Table 5; $B_1=0.25$, $U_1=0.3$, $D_1=0.45$ & $B_2=0.669$, $U_2=0.0$, $D_2=0.331$ Applying the equations:

$$\beta = (1 - 0.25 * 0.331 - 0.669 * 0.45) = 0.616$$

$$B_{12} = (0.25 * 0.669 + 0.25 * 0.0 + 0.669 * 0.30) /$$

$$0.616 = \underline{\underline{0.597}}$$

The beliefs in the other classes are small, for example the combined belief that the CL class is 1.0–2.0 keq ha⁻¹ year⁻¹ is 0.013. As the hypotheses are *independent* the Beliefs *do not sum to one*. In this case the inclusion of knowledge about the vegetation community at the site will lead us to revise the CL downwards from the national estimate. If the more traditional Bayesian statistic is used (allocating all uncertainty to disbelief) the conclusion to revise the CL downwards is stronger (belief in CL class 0.2–0.5 is 0.546 and in CL class 0.5–1.0 is 0.403).

4 Conclusions

Uncertain, incomplete and contradictory information is common in all areas of environmental science. Decision makers and land managers want estimates specific to a particular designated site but they lack resources to make the required measurements. Data collected to assess national or super-national concerns will not be ideal for site specific concerns. Endorsement Theory allows incomplete information to be assessed and combined in a way that makes expert opinion explicit, traceable and transparent; for each piece of evidence we know where it came from, what “weight” it was given by the expert and how the evidence was combined to produce an endorsement. The reasons for the endorsement of any hypothesis can be clearly identified and tested against other opinions. There are a number of technical issues concerned with the use of Endorsement Theory that need further investigation, but perhaps more important is the fact that non-numeric methods like Endorsement Theory are not widely used, and the extent to which there will be

cultural and organisational resistance to their use needs to be investigated. The Dempster–Shafer formalism allows the combination of uncertain information when the probability model can be assumed to be complete. Combining the two approaches provides a useful tool for combining variable and incomplete information to provide a better estimate of CL for a site.

Acknowledgements Some of the ideas expressed in this paper were developed during a contract funded by the UK Environment Agency, project manager, Dr. Rob Kinnersley. We wish to thank the referees for important pointers in making this paper more readable.

References

- Calver, L. J., Cresser, M. S., & Smart, R. P. (2004). Tolerance of *Calluna vulgaris* and peatland plant communities to sulphuric acid deposition. *Chemistry and Ecology*, 20, 309–320.
- Cohen P. R. (1985). *Heuristic reasoning about uncertainty: An artificial intelligence approach*. Boston, MA: Pitman.
- Comber, A. J., Law, A. N. R., & Lishman, J. R. (2003). A comparison of Bayes’, Dempster–Shafer and Endorsement theories for managing knowledge uncertainty in the context of land cover monitoring. *Computers, Environment and Urban Systems*, 28, 311–327.
- Dempster, A. P. (1967). Upper and lower probabilities induced by a multi-valued mapping. *Annals of Mathematical Statistics*, 38, 325–339.
- Hall, J., Ulyett, J., Heywood, L., Broughton, R., & Fawehinmi, J. (2004). The National Critical Loads Mapping Programme Phase IV. Final report to Defra: July 2001–June 2004 (Contract EPG 1/3/185).
- Hornung, M., Bull, K. R., Cresser, M., Hall, J., Langan, S. J., Loveland, P., et al. (1995). An empirical map of critical loads for acidity in Great Britain. *Environmental Pollution*, 90, 301–310.
- Loveland, P. J. (1991). The classification of the soils of England and Wales on the basis of mineralogy and weathering – the Skokloster Approach. A report to the Dept. of the Environment under Research Contract Reference No. PECD 7/12/44.
- Rodwell, J. S. (Ed.) (1991). *British plant communities*. (vol 5) Cambridge, UK: Cambridge University Press.
- Shafer, G. (1976). *Mathematical theory of evidence*. Princeton, N.J.: Princeton University Press.
- Soil Survey of England and Wales (1983). Legend for the 1:250,000 Soil Map of England and Wales. Soil Survey of England and Wales. Rothamsted Experimental Station, Harpenden, Herts, AL5 2JQ.
- Tangestani, M. H., & Moore, F. (2002). The use of Dempster–Shafer model and GIS in integration of geoscientific data for porphyry copper potential mapping, north of Shahr-e-Babak, Iran. *International Journal of Applied Earth Observation and Geoinformation*, 4, 65–74.

Why Critical Loads of Acidity and N for Soils Should be Based on Pollutant Effective Concentrations Rather Than Deposition Fluxes

Malcolm S. Cresser

Received: 17 June 2005 / Revised: 6 November 2005 / Accepted: 3 December 2005 / Published online: 11 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Numerous assumptions have been made over the past 17 years when calculating critical loads for soils, both for acidity (based upon base cation steady state mass balances (SMB)) and for N (eutrophication, based upon N mass balances), often without *all* the assumptions being explicitly stated. The tacit assumptions that the author believes to be implicit in the SMB approach are critically reviewed, with particular reference to upland regions where slope processes are highly significant. It is concluded that many of them cannot be justified, especially those that involve ignoring many key processes known to be important to biogeochemical cycling and soil evolution in upland catchments. The evidence presented suggests that critical loads of acidity and of N for soils should be based upon effective pollutant and, for acidity, also effective base cation deposition concentrations, rather than upon pollutant deposition fluxes. This is because of the dominant role of cation exchange equilibria, rather than weathering rate, in regulation of the pH and base status of the more acidification-sensitive soils, and because of the importance of transport down slope of base cations, alkalinity and N species.

Keywords critical load · acidity · nitrogen deposition · effective concentration · flux · slope processes · soil · uplands · cation exchange

1 Introduction

The concepts underpinning our approach to critical loads of acidity for soils were first formulated in their most widely recognisable form at a UN-ECE workshop held at Skokloster, Sweden, in 1988 (Nilsson & Grennfelt, 1988). Put very simply, to use critical load (CL) as a pollution management tool, the simplifying assumption was made initially that all the alkalinity (a) generated in soils or present in freshwaters is available for neutralising acidifying pollutant inputs (p). It was then assumed that, provided (a) > (p), no “damage” to the ecosystem would occur. In practice, base cation (BC) weathering rates (BC_w) are used as a surrogate for alkalinity, and allowance is made for plant BC uptake (BC_u) and deposition (BC_{dep}). Thus, according to section 5.3.2 of the current critical loads modelling and mapping manual (ICP, 2004), BC leaching (BC_{le}) is given by:

$$(BC_{le}) = (BC_{dep}) + (BC_w) + (BC_u)$$

This steady state mass balance approach (SMB) has been widely used across Europe. The weathering rates used initially at Skokloster were based predominantly upon calculations of the excesses of annual BC fluxes

M. S. Cresser (✉)
Environment Department, University of York,
Heslington, York YO10 5DD, UK
e-mail: msc5@york.ac.uk

leaving catchments over corresponding atmospheric BC flux inputs, although other methods are now also widely used (see section 5.3.2.3 of the mapping manual). Most of these are, however, “fine-tuned” to give results in agreement with catchment study-based weathering rates.

For speedy delivery of CL maps at a European scale, this approach was potentially very attractive to policy makers; all that was required was a data set for the spatial variability of soil weathering rates across Europe, based upon informed estimations. In spite of the reservations of the assembled scientists at Skokloster, which have been documented elsewhere (Cresser, 2000), the steady state BC mass balance approach was used through the 1990s for calculation of CLs of acidity for soils (e.g. Sverdrup, de Vries, & Henriksen, 1990; Hornung et al., 1995). Over more recent years, the approach has been extended by attempting to use the BC mass balance approach to predict the BC:Al or Ca:Al ratios that would be likely to cause root damage to plant species of interest (e.g. Langan et al., 2004 and refs. therein). For nitrogen critical loads, section 5.3.1 of the mapping manual still suggests that the SMB approach is a useful starting point “for calculating critical loads of nutrient nitrogen (eutrophication).” Five key assumptions are listed, but the influence of slope and N species transfer in laterally flowing water is not mentioned at all.

Some of the numerous simplifying assumptions associated with these approaches have been criticised before by the author (Cresser, 2000), but that earlier critical review missed some of the fundamental flaws associated with the whole approach, especially when it is applied in upland areas. Therefore the purpose of this short critique is to consider the assumptions still being routinely made, sometimes tacitly, in CL calculations for soils, and whether any of the assumptions are sufficiently inappropriate to invalidate the CL approach, especially in upland catchments where many of the most acidification-sensitive soils are to be found. Assumptions about nutrient inputs/outputs all being vertical are clearly invalid, yet section 5.3 of the mapping manual assumes “percolation is constant throughout the soil profile and occurs only vertically.” This and other major assumptions that appear to the author to be implicit for the SMB approach to be valid, and therefore assumptions that need to be considered carefully, are

listed below, as well as important misconceptions about sea salt inputs and their effects. Each will be discussed briefly in turn:

- In uplands, if alkalinity is transferred down slope naturally with lateral water flow under sub-critical load deposition conditions, it is of no consequence to soil chemistry or the ‘health’ of biota down slope.
- Pre-pollution, alkalinity production played no role in regulation of ‘natural’ soil pH or base status, so it is all therefore available for neutralising acid inputs.
- Sum of base cations may be used as a surrogate for HCO_3^- , so catchment study-based weathering rates can be used to help set CLs of acidity for soils.
- It doesn’t matter where in the soil profile HCO_3^- is produced (i.e. weathering anywhere down to rooting depth is an exploitable buffering resource).
- The land surface is horizontal, so under a horizontal square meter the mass of soil to a specified depth doesn’t change with slope.
- Marine aerosol-derived deposition doesn’t need to be considered because it is a natural phenomenon (an assumption in sections 5.3.2.1 and 5.3.2.3 of the mapping manual).
- All rain passes through more-or-less homogenous soil, and no acid or N flux runs off of bare rocks and into soil down slope.
- “Damage” to soil or associated biota doesn’t vary with concentrations of acidifying pollutants, or concentrations of ions in soil solution, only with deposition fluxes.

2 Discussion of the Assumptions Made

2.1 In Uplands, if Alkalinity is Transferred Down Slope Naturally with Lateral Water Flow Under Sub-critical Load Deposition Conditions, it is of No Consequence to Soil Chemistry or the ‘Health’ of Biota Down Slope

This is obviously incorrect in most upland areas, especially during precipitation episodes. In fact, it is true only when weathering is negligible or CL is equalled or exceeded. Lateral alkalinity flow keeps soil pH and BS% higher on lower slopes (a concept found in most basic soil science texts). These, often very large, lateral fluxes of alkalinity in through-flow water cannot sensibly be ignored when CLs are

quantified using the (a) > (p) concept. Supporters of the current SMB approach might argue that, at steady state equilibrium, and if critical load was equalled or exceeded, there eventually would be no lateral movement of alkalinity anywhere in the rooting zones of soils in the catchment. They would thus argue that soils at the tops of slopes would be damaged first, and the damage would, all be it slowly, then “spread” down slope. However, under pristine conditions the BC and alkalinity fluxes passing through upland soils may massively exceed the corresponding fluxes estimated by assuming that all water infiltrates vertically. This would have a beneficial effect on soil base status down slope for thousands of years (Edwards, Creasey, Skiba, Peirson-Smith, & Cresser, 1985). The “damage” being done to soils at the foot of slopes at the “final” equilibrium would thus be far greater than that done up slope. Clearly what we need to do is to find a way to take the decline in alkalinity moving laterally down slope in response to acid deposition into account. Setting critical loads based on what we think might happen to soils down slope in a few thousand years carries the precautionary principle to the extreme.

Only when the lateral flow of alkalinity approaches zero can the effects of acid deposition on soil chemistry start to become similar on upper and lower slopes. This however corresponds to a system where in all upslope soils, cation exchange reactions must be regulating surface soil chemistry rather than weathering rates. Under these conditions cation relative concentrations and total mobile anion concentrations together regulate soil solution chemistry and its biotic effects. *Concentrations* matter rather than fluxes per se.

For acidifying peat soils it has long been well known that ion exchange equilibria regulate the surface soil chemistry (e.g. Skiba & Cresser, 1989). Peat equilibrates with both precipitation inputs and drainage water. Thus effective input base cation concentrations and effective precipitation pH should equal drainage water base cation concentrations and pH. “Effective” concentration is defined as input flux divided by runoff, and has been used to quantify CLs for peat soils in the UK (Hornung et al., 1995). For ombrotrophic peats in the UK, effective acidifying pollutant concentrations have always been used, rather than deposition fluxes, to quantify CL values. However, it has been demonstrated that the surface organic horizons of podzols adjacent to peat soils

display similar pH characteristics to the peat upper horizon; both have their chemistry regulated by cation exchange equilibria involving primarily Ca^{2+} and H^+ (White, Dawod, Cruickshank, Gammack, & Cresser, 1995). The author therefore suggests that effective pollutant concentrations, and not annual deposition fluxes, should be more appropriate for setting critical loads for acidification-sensitive mineral soils, just as they have for peat soils.

2.2 Pre-pollution, Alkalinity Production by Weathering Played No Role in Regulation of “Natural” Soil pH

Section 5.2.2 of the mapping manual states that: “the critical load is effectively the base cation weathering rate, with the leaching of acid neutralizing capacity (ANC) set to zero.” This implies that excess HCO_3^- is available for neutralizing acidity inputs, without causing any damage to soils down slope. This is clearly not true. Pre-pollution, soil type, and hence soil horizon pH and BS%, depended on weathering rate and topography and the other factors of soil formation. Much HCO_3^- was “used up” in regulation of natural (pre-pollution) soil pH etc., so it is not available for neutralizing acid deposition. Even where weathering is still significant in surface horizons, we shouldn’t assume the weathering products are “all available” to neutralise incoming acidity, especially if rates are based on BC annual fluxes in rivers. Wherever lateral flow is significant, clearly the flux of HCO_3^- passing through a m^3 of soil may be very large compared with the acid deposition flux per m^2 of horizontal surface.

2.3 BC Can be Used as a Surrogate for HCO_3^- , so Catchment Study-based Weathering Rates Can be Used to Set CLs of Acidity for Soils

From weathering rate estimates based upon catchment input/output balances, there is clear evidence (Stutter, Smart, & Cresser, 2002) that much alkalinity generated in catchment soils is used up already by acid deposition (not a problem) and also by neutralisation of organic acidity (a problem if not adequately considered). These authors found that the annual flux of alkalinity in each of 36 Scottish upland rivers was always substantially less than the sum of annual BC fluxes (both expressed on a moles of charge basis).

The difference was due to the Ca and Mg associated with non-marine sulphate and with soluble organic matter. Organic complexation of these two elements can consume a lot of the weathering-derived alkalinity therefore (i.e. by partial neutralisation of organic acidity). This concept is embraced in section 5.3.2 of the mapping manual, when cation/anion balances are used. Unfortunately when catchment-based weathering rates based on sums of BC were used at Skokloster for setting provisional CL values, little or no thought was given to the spatial or temporal heterogeneity of organic anion production relative to that of BC weathering in catchments. This could mean that buffering capacity is being seriously overestimated for soils in some areas of a catchment, and underestimated in others. As mentioned in the introduction and in section 5.3.2.3 of the mapping manual, there are many other methods for making “guestimates” of weathering rates. However, none is sufficiently accurate not to cause substantial uncertainty if used to set values of critical loads of acidity.

There is an additional problem associated with the use of catchment study-based base cation weathering rates. The rock composition of the riparian zone has a disproportionately large influence upon surface water quality compared with that of catchment rocks as a whole. Indeed, water quality under diverse flow regimes can be reliably modelled from flow-path weighted riparian zone rock chemistry (Cresser et al., 2000; Smart et al., 2001). Thus it is highly probable that many of the catchment study-based weathering rates advocated for setting CLs at Skokloster were highly inappropriate for soils upslope, beyond the riparian zone. Yet such rates have significantly influenced the “fine tuning” of weathering rates estimated by the modelling methods suggested as alternative approaches in section 5.3.2.3. of the mapping manual.

2.4 It Doesn't Matter Where in the Soil Profile HCO_3^- is Produced

In acidification-sensitive soils, rooting depth (and many fine roots) are often close to the soil surface. Mixing between horizons is often negligible in such soils, which is why horizon delineation is often so clear. In many podzols, weathering is negligible in the surface horizons, and soil chemistry depends upon cation exchange equilibria, not upon weathering rate.

Soil pH near the surface depends upon acidifying pollutant and base cation deposition effective concentrations, as demonstrated by White et al. (1995), not just on fluxes, because precipitation and soil solution both equilibrate with the soil solid phase, as discussed earlier for peat soils.

2.5 The Land Surface is Horizontal, so Under a Horizontal m^2 the Mass of Soil to a Specified Depth Doesn't Change

Clearly this is not true; e.g. if the slope is 45° , the mass of weathering soil per horizontal m^2 increases by a factor of *ca.* 1.4. However, on such a slope lateral flow of acid and/or alkalinity may be so great that the concept of balancing acidity and weathering rate fluxes is almost meaningless anyway.

2.6 Sea-salt Deposition Doesn't Influence Soil pH, Base-status, etc

The mapping manual (Sections 5.3.2.1 and 5.3.2.3) states very clearly that sea salt BC inputs should be excluded from critical load calculations because they are not of anthropogenic origins. Comparison of base cation inputs from the atmosphere and from weathering (the latter estimates derived from the Profile model) for 21 *Calluna* moorland podzol soils across N.E. Scotland clearly showed that, except for a very base-rich catchment, atmospheric inputs of base cations, especially of sodium, substantially outweighed inputs from mineral weathering (Stutter, Langan, & Cresser, 2003). Therefore we might expect precipitation chemistry predominantly to regulate soil solution chemistry and drainage water chemistry in catchments with very low biogeochemical weathering rates. Stutter et al. (2003) very clearly showed that this was definitely the case, and it follows that ion-exchange, which depends upon cation effective concentrations, is the dominant controlling process for soil chemistry. One important consequence of this is that atmospheric deposition of marine-derived sea salts must be included in attempts to predict pH of acidification-sensitive soils from deposition and weathering-rate data. If this is not done there is no significant correlation between, for example, soil pH and exceedance of CL of acidity for Scottish *Calluna* moorland podzols; if it is done, the pH of L/F/H, A/E and B horizon soils are all significantly correlated

with exceedance (White, Cresser, & Langan, 1996). This is firm evidence that CL values should be based upon consideration of ion exchange equilibria, and hence on relative effective concentrations of cation inputs, rather than deposition fluxes of acidifying pollutants.

2.7 All Rain Passes Through More-or-less Homogenous Soil, and No Acid Runs Off of Bare Rocks and Into Soil

This is not true in many pollutant effect-sensitive upland catchments. High acid and N fluxes enter soils below rock outcrops, but over many years the author has been unable to find any signs of greater visible damage to vegetation in such areas. This supports the idea that effective concentration is more important than total acid flux entering a soil, because acid fluxes may be very high indeed locally below rock outcrops. Any vegetation changes observed by the author seem to have been more obviously associated with the greater water flux below outcrops.

The author and colleagues (Smart, Cresser, Calver, Clark, & Chapman, 2005) have recently developed a model that allows prediction of both spatial and temporal leaching of nitrate into sub-catchment streams of the Nether Beck catchment in the English Lake District. In the model, the % outcropping rock in each catchment's area is a key controlling variable, confirming N fluxes are greatly enhanced below rock outcrops. But in spite of the massively enhanced N fluxes at such local sites, there is no evidence of local N-induced damage in the author's experience. This is really hardly surprising, because we would expect plant communities to respond to concentrations in soil solution, and not to the total deposition flux passing, often quite rapidly during storms, through soils.

2.8 “Damage” to Soil Doesn’t Depend Upon Concentrations of Acidifying Pollutants, Only Upon Deposition Fluxes (by Analogy with a Simple Acid-base Titration)

In spite of the simplicity of this analogy, it has to be pointed out that you don't do a titration without swirling the flask to homogenise the distribution of reactants! The heterogeneity of soils in upland catchments is such that it is naïve to ignore it. Yet we tacitly assume it's acceptable to average weathering

rate over 3-dimensional space over large horizontal (km) distances. This is clearly not sensible if we wish to protect plant communities across a landscape. The surface soil heterogeneity needs to be better taken into account.

2.9 Are There Any Other Problems We Need To Consider?

Flushes of sulphuric or nitric acid into rivers at high discharge via lateral flow during episodes mean that this part of the total acid input was not neutralised in soils. This means that the input acid flux would be an overestimate of the flux causing “surface soil damage” in such conditions. If we use effective concentrations to set critical loads of surface soils, these mineral acid outputs are not an issue.

3 Conclusions

From the above discussion it is very obvious that there are several fundamental flaws associated with applications of the current CL of acidity approach for soil. They are:

- Slope processes and lateral alkalinity fluxes seriously limit the value of the current CL approach, especially in many upland areas of northern Europe.
- More research is needed into how explicitly BC weathering rate estimates are used in the setting of CL values.
- We need to take spatial differences in soil chemistry down soil profiles into account more appropriately.
- The uplands are not flat and often contain substantial areas of outcropping rock, and this matters for N and S cycling and when setting N and acidity CLs.
- It is not justifiable to ignore sea-salt inputs in setting CL of acidity values as they can substantially influence soil pH (and hence soil biology) in acidification-sensitive soils.
- Cation exchange is more important than weathering in the many, more sensitive, upper horizon soils.
- Relative effective cation concentrations and mobile anion concentrations govern soil chemistry, and hence the incidence and extent of damage, in acidification-sensitive soils, not deposition fluxes per se. Also plants respond to concentrations rather than fluxes. They probably could be more sensibly

used to set empirical critical loads that are more conceptually sound.

In the author's opinion, the failure to take these limitations into account is a serious limitation to the reliability of current environmental management strategies in many parts of upland Europe. For N critical loads, even the empirical critical loads approach probably should be reconsidered, bearing in mind impacts of slope processes and of precipitation amount on N cycling, before it is routinely applied in upland areas.

Acknowledgements The author thanks NERC and DOE/DETR/DEFRA for support over 25 years, and Richard Smart, Mike Billett, Tony Edwards, Mike Hornung, Chris Evans, Pippa Chapman, Colin Neal, Catherine White, Simon Langan, Brian Reynolds, Bridget Emmett, Harald Sverdrup, Andy Crowe, Matt Clark, Andy Wade, Chris Soulsby, Louise Calver, Kathryn Emmerson and Nayan Ahmed for many helpful and stimulating discussions that contributed to the formulation of the ideas in this paper.

References

- Cresser, M. S. (2000). The critical loads concept: Milestone or millstone for the new millennium? *Science of the Total Environment*, 249, 51–62.
- Cresser, M. S., Smart, R., Billett, M. F., Soulsby, C., Neal, C., Wade, A., et al. (2000). Modelling water quality for a major Scottish river from catchment attributes. *Journal of Applied Ecology*, 37(Supplement 1), 171–184.
- Edwards, A. C., Creasey, J., Skiba, U., Peirson-Smith, T., & Cresser, M. S. (1985). Long-term rates of acidification in UK upland acidic soils. *Soil Use and Management*, 1, 61–65.
- Hornung, M., Bull, K., Cresser, M., Hall, J., Langan, S., Loveland, P., et al. (1995). An empirical map of critical loads for soils in Great Britain. *Environmental Pollution*, 90, 301–310.
- ICP (2004). Modelling and Mapping Manual, available on the web at: <http://www.icpmapping.org/html/manual.html>, accessed October 2005.
- Langan, S. J., Hall, J., Reynolds, B., Broadmeadow, M., Hornung, M., & Cresser, M. S. (2004). The development of an approach to assess critical loads of acidity for woodland habitats in Great Britain. *Hydrology and Earth System Sciences*, 8, 355–365.
- Nilsson, J., & Grennfelt, P. (Eds.) (1988). Critical loads for sulphur and nitrogen: Report 15. Copenhagen: Nordic Council of Ministers.
- Skiba, U., & Cresser, M. (1989). Prediction of long-term effects of rainwater acidity on peat and associated drainage water chemistry. *Water Research*, 23, 1477–1482.
- Smart, R. P., Cresser, M. S., Calver, L. J., Clark, M., & Chapman, P. J. (2005). A novel modelling approach for spatial and temporal variations in nitrate concentrations in an N-impacted UK upland river network. *Environmental Pollution*, 136, 63–70.
- Smart, R. P., Soulsby, C., Cresser, M. S., Wade, A. J., Townend, J., Billett, M. F., et al. (2001). Riparian zone influence on stream water chemistry at different spatial scales: A GIS-based modelling approach, and example for the Dee, NE Scotland. *Science of the Total Environment*, 280, 173–193.
- Stutter, M., Langan, S., & Cresser, M. S. (2003). Weathering and atmospheric deposition signatures of base cations in upland soils of NE Scotland: Their application to critical load assessment. *Geoderma*, 116, 301–324.
- Stutter, M., Smart, R., & Cresser, M. S. (2002). Calibration of the sodium base cation dominance index of weathering for the River Dee Catchment in north-east Scotland. *Applied Geochemistry*, 17, 11–19.
- Sverdrup, H., de Vries, W., & Henriksen, A. (1990). *Mapping critical loads: A guidance to the criteria, calculations, data collection and mapping of critical loads; Report Nordic 1990–1998*. Copenhagen: Nordic Council of Ministers.
- White, C. C., Cresser, M. S., & Langan, S. J. (1996). The importance of marine derived base cations and sulphur in estimating critical loads in Scotland. *Science of the Total Environment*, 177, 225–236.
- White, C., Dawod, A., Cruickshank, K., Gammack, S., & Cresser, M. (1995). Evidence for acidification of sensitive Scottish soils by atmospheric deposition. *Water, Air and Soil Pollution*, 85, 1203–1208.

The Applicability of National Critical Loads Data in Assessing Designated Sites

Jane Hall · Jackie Ulyett · Richard Wadsworth ·
Brian Reynolds

Received: 17 June 2005 / Revised: 11 January 2006 / Accepted: 12 February 2006 / Published online: 9 January 2007
© Springer Science + Business Media B.V. 2007

Abstract Critical loads have been successfully used within Europe in the development of effects-based policies for pollution abatement, including the Second Sulphur Protocol and the Protocol to abate acidification, eutrophication and ground-level ozone (CLRTAP, 1979). This success has encouraged the UK Environment Agency and Conservation Agencies to use the national critical load maps as a screening tool in assessing the threats from acidification and eutrophication to designated (Natura 2000) sites. The UK maps of critical loads are based on national-scale data sets appropriate for national-scale assessments, and were never intended for use at the site-specific level. Site-based assessments are often targeted at Special Areas of Conservation, a sub-set of the UK Natura 2000 sites. The spatial data available includes the boundaries of the sites but not the location of the designated features. Ancillary data is variable from one site to another; habitat types may be described in detail with cross-reference to classes of the National Vegetation Classification (NVC: Rodwell, 1991 et seq),

but information available on soils and geology is generalised and has not been related to the habitats or species being protected. Hence it can be difficult to relate the individual sites to the national maps, even where appropriate to do so. This paper examines the underlying uncertainties in the national critical load maps showing how the maps could give misleading results if used for site-specific assessments. It also includes advice on how to determine when the national data may be appropriate as a policy-tool at the site-level.

Keywords critical loads · designated sites · endorsement theory · national vegetation classification · policy · acidification · eutrophication

1 Introduction

Critical loads (CL) have proved to be a useful tool in the development and review of national (eg, UK Air Quality Strategy (DETR, 2000)) and international (eg, Protocols (CLRTAP, 1979)) policies to abate the pollutants responsible for acidification and eutrophication. The UK maps of acidity and nutrient nitrogen CL have been developed using national databases of soils and habitat information (Hall et al., 2003, 2004a). These maps provide national-scale pictures of the areas and habitats at risk from the potential harmful effects of excess acid or nitrogen deposition.

J. Hall (✉) · J. Ulyett · R. Wadsworth
Centre for Ecology and Hydrology,
Monks Wood, Abbots Ripton,
Huntingdon PE28 2LS, UK
e-mail: jrha@ceh.ac.uk

B. Reynolds
Centre for Ecology and Hydrology,
Orton Building, Deiniol Road,
Bangor, UK

The EU Habitats Directive (EU, 1992) requires measures to be taken to maintain or restore to favourable conservation status, habitats and species of wild flora and fauna, listed in the Annexes to the Directive. In England and Wales the Environment Agency and Conservation Agencies are charged with the task of assessing the potential threats from acidification and eutrophication to the UK's designated Natura 2000 sites. The data collated for these sites include the lists of designated habitats and species and a general description of the site characteristics. Generally there is insufficient data to calculate a site-specific CL, and unfortunately, information on soils, geology and other descriptive information is generalized and not related to the designated features. Hence the national maps have been used as a "screening tool" even though they were never intended for assessments at the site-specific scale and may give misleading results. As a consequence the UK Environment Agency has funded research to provide guidance on the use of the national maps or alternative approaches for carrying out site-level assessments.

2 Background to the National Critical Load Maps

The national acidity and nutrient nitrogen CL maps are based on internationally agreed methods (UBA, 2004) and on the best available data to provide national coverage. Critical loads are calculated and mapped for UK Biodiversity Action Plan Broad Habitats sensitive to acidification and eutrophication. The maps of acidity CL for terrestrial non-woodland habitats are based on the UK acidity CL for soils. Values have been derived separately for peat and non-peat soils; CL for non-peat soils are based on the mineralogy and weathering rate (Hornung et al., 1995). This method is inappropriate for peat soils, for which the CL are based on a critical soil solution pH (Calver, Cresser, & Smart, 2004; Hall et al., 2004a). The maps for woodland habitats are derived using a UK formulation of the simple mass balance model (Langan et al., 2004; Hall et al., 2004a) and incorporate the soil acidity CL values in setting the base cation weathering component. There are a number of limitations and uncertainties in the national CL data, for example:

- (1) The soils data are based on the dominant soil association within each 1×1 km grid square; other soil associations (or sub-dominant series within them) may be more or less sensitive to acidification or eutrophication and have lower or higher critical loads.
- (2) The 1×1 km soils databases are derived from 1:250,000 scale soil maps, therefore not all soil types within each 1×1 km grid square will necessarily be represented.
- (3) The habitat distributions are based on a combination of 1×1 km summary land cover information, species distribution data mapped at 10×10 km resolution and ancillary data sets at a range of scales (Hall et al., 2003). Hence the national habitat-specific CL maps will not necessarily include all small areas of sensitive habitats.
- (4) Features may be designated *because* they are rare or infrequent; they are therefore difficult to map.
- (5) Within the CL models some input parameters, such as the uptake and removal of base cations and nitrogen resulting from the harvesting of productive forestry are based on data for a limited number of sites.
- (6) The critical chemical criteria on which the national CL maps are based (eg, the critical molar ratio of calcium to aluminium in soil solution) may be inappropriate for the protection of the designated feature(s) on the site, but suitable criteria may not be available.

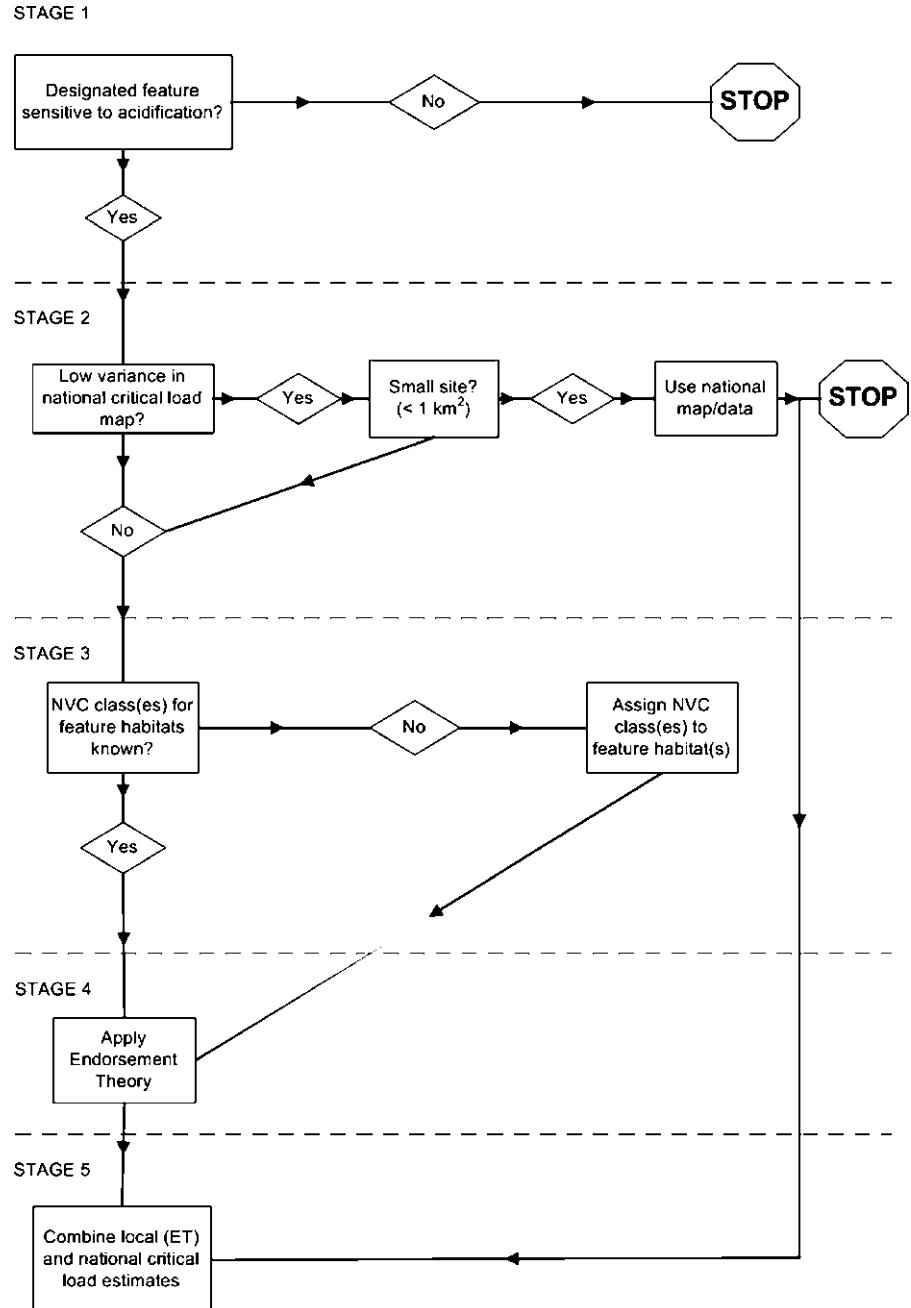
A formal assessment of the uncertainties in the national CL data has been carried out (Hall, Ullyett, Heywood, Broughton, & Fawehinmi, 2004b) and a comparison of the uncertainties at the national and local scales is currently being undertaken (Heywood, Skeffington, Whitehead, & Reynolds, (this issue); Skeffington et al., 2005). Despite their limitations the UK CL maps provide an adequate picture of the sensitivity of habitats to acidification and eutrophication both nationally and regionally. Critical load maps have been widely accepted by policy-makers, partly because they are simple to understand as well as providing an effects-based approach to pollution abatement. They are routinely used by the UK Department for Environment, Food and Rural Affairs to assess the potential impacts of future emission and deposition scenarios and they form the official UK data set used for activities under the CLRTAP.

However, at the local or site-specific scale the maps may give misleading results if they are not used with care and the associated uncertainties taken into account. The following sections present and discuss a practical framework aimed at guiding the policy maker in the use of national CL maps or viable alternatives.

3 A Framework for Assessing Designated Sites

In an attempt to bridge the gap between the uncertainties in the use of the national-scale data and the lack of site-specific data, we propose a hierarchy (Fig. 1) to consider where, when and how the national data may be used, or an alternative site-specific

Fig. 1 Proposed framework for assessing designated sites



approach. The approach is illustrated in terms of acidity below.

3.1 Stage 1: Assessing Whether the Designated Feature is Sensitive to Acidification

In the UK, Special Areas of Conservation (SACs) and Specially Protected Areas (SPAs) represent the “Natura 2000” sites, designated for protection under the EU Habitats Directive. Each site is designated to protect one or more features (habitats or species). The “Natura 2000 standard data form” lists these features in terms of the Habitats Directive Annex 1 Habitats or Annex II Species. At this stage the user needs to determine if the designated feature is sensitive to acidification; this may be done by consulting relevant experts or the literature (eg, UK Biodiversity Action Group, <http://www.ukbap.org.uk> or the UK Air Pollution Information System, <http://www.apis.ac.uk>). If the designated feature is not sensitive to acidification then there is no requirement to determine an appropriate CL or progress to the next stage.

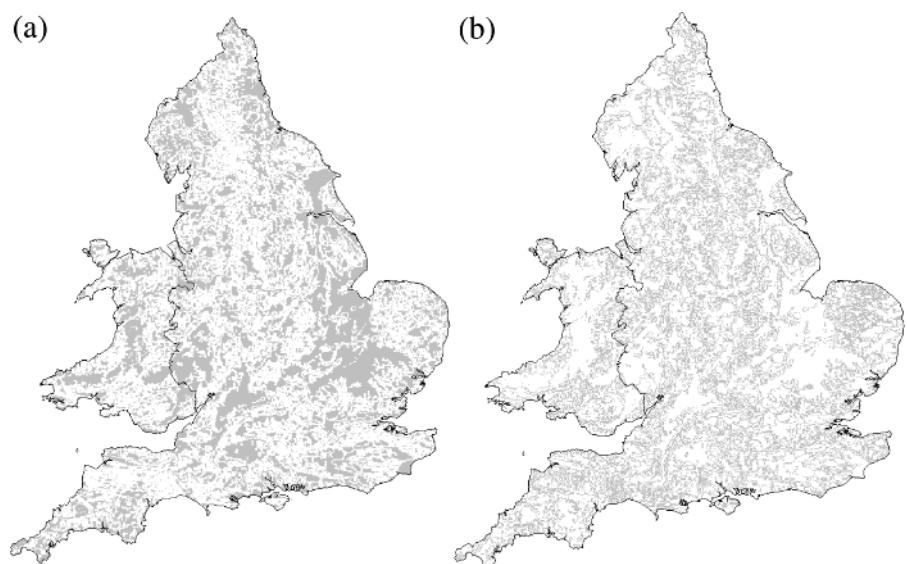
3.2 Stage 2: Using the National Critical Loads Map

In this stage the “variance” in CL values within each 1×1 km grid square is examined (the national maps have been described in Section 2). This is demonstrated by the maps in Fig. 2 which are based on the soil acidity CL values only, rather than national habitat-specific CLs. In this way the CL is set to

protect the soil upon which a habitat may occur or depend. The link to habitat in terms of vegetation community comes into Stage 3 of the framework. The maps in Fig. 2 compare the CL values for all soil associations in each 1×1 km grid square. The maps identify areas where (a) CL values are all the same; (b) CL for a sub-dominant soil is the lowest. It should be noted that this map does not include those 1×1 km² dominated by peat soils. Therefore, if a designated site is in an area (or a 1×1 km²) where all the critical load values are the same for all soil types (Fig. 2a), there can be said to be low variance in the critical load.

If the site is small (<1 km²), and there is no variance in the CL, then the national value can be used, although the uncertainties in the national map (Section 2) should still be taken into consideration. If the site is larger there are several additional issues to consider. Firstly, the grid reference provided for each site is for the centre point, and the site may consist of one or many adjacent or non-adjacent land parcels. Therefore this centre point may not be representative of the site as a whole, in terms of the soil CL values, or of the habitat or species for which the site is designated. For example, the CL may vary not only within each 1×1 km² but also from square to square within a site. If the within-square variance in critical loads is low for each square the site covers, the values for all squares within the site could be extracted, and if done within a Geographical Information System, an area-weighted mean CL could be determined. But as

Fig. 2 Variance in soil acidity critical loads **a** critical loads for dominant and sub-dominant soil the same, **b** Sub-dominant soil most sensitive (lowest critical load)



large sites may contain a wide variety of soil and habitat types (as well as designated features) such an area-weighted mean value could also be inappropriate. If appropriate data are to be extracted from the national map then it is important that the locations of the designated features are known; currently this information is not readily available outside the Conservation Agencies and in some cases may not even exist.

If the variance in the critical load values for each $1 \times 1 \text{ km}^2$ is high then it is important that the relationships between the soils and the habitats are known or can be inferred. In such instances we recommend moving onto Stage 3.

3.3 Stage 3: Using the National Vegetation Classification

The National Vegetation Classification (NVC, Rodwell, 1991 et seq) is frequently used in the UK to describe natural and semi-natural vegetation communities. This stage of the hierarchy is aimed at defining the designated features in terms of NVC classes, required for Stage 4. The SAC site information held by the Joint Nature Conservation Committee (<http://www.jncc.gov.uk>) typically includes descriptions of the designated Annex I Habitats in terms of NVC classes. Therefore for many sites the designated features are already related to an NVC class or classes; where this is not the case the user can consult a relevant expert or the National Biodiversity Network Habitats Dictionary (<http://www.nbn.org.uk/habitats>) which provides information on the relationships between Annex 1 Habitats and NVC classes.

3.4 Stage 4: Applying Endorsement Theory

An Endorsement Theory approach has been developed by Wadsworth and Hall (this issue) to determine CL for individual NVC classes. Endorsement Theory (Cohen, 1985) is ideally suited to problems where data are incomplete and the evidence uncertain, as is the case with designated sites which tend to lack detailed information relating the location of habitats or species to their associated soil or geology types. The Endorsement Theory method uses all available published information on the soils and geology for each NVC class (contained in the five volumes of Rodwell, 1991 et seq) and relates this to the soils and

geology information used in setting critical loads (Loveland, 1991). It uses a “symbolic” (rather than numeric) approach to derive an evidence based endorsement for each “CL class” (identical to the class ranges used by Hornung et al., 1995). An endorsement can be: “definitive,” “confident,” “likely,” “weak” or “very weak” or none. The amount of information available for each NVC community is very variable so for some communities no CL class receives more than a “very weak” endorsement, other communities are better described and a stronger endorsement may be given to one or more CL classes. The authors have designed a database that generates the CL endorsements for any terrestrial NVC class (that is, excluding the aquatic communities).

3.5 Stage 5: Combining Local (Endorsement Theory) and National Critical Load Estimates

There are uncertainties in the estimate of CL whether they are taken from the national map or from the “local” estimate based on Endorsement Theory. Two approaches for combining the estimates are possible; symbolic and numeric.

A symbolic approach can be considered as a form of quality assurance. The endorsement for each CL class (for the site relevant NVC communities) can be compared to the national estimate. The degree to which they agree (or conflict) can be used to decide whether further investigation or screening is required. For example if the NVC community had a “definitive” or “confident” endorsement for the same CL class as the national data, that might be considered good confirmation. If there was only a “weak” or “very weak” endorsement for the CL class, but no other class had a strong endorsement then the national estimate could be considered plausible, where there is a strong endorsement for a different CL class that would indicate further investigation was required.

In a numeric approach the different levels of endorsements need to be converted to “probabilities”. This is the same process as deciding on the number of endorsement categories and their labels, ie, it is an expert opinion. In this case our expert considers that a “definitive” endorsement is equivalent to a 0.9 probability. In an analogous manner the CL variance map can be used to provide an estimate of confidence in the national CL value. The numeric values may then be combined using a Dempster-Shafer formalism

(Dempster, 1967; Shafer, 1976) as this enables an explicit representation of the uncertainty. Dempster–Shafer is mathematically equivalent to Bayesian statistics if the uncertainty is zero, and like Bayes it is essentially concerned with the revision of belief following additional information. A worked example is given in Wadsworth and Hall (this issue).

4 Conclusions

There are uncertainties in using national CL maps at the national, regional and local scales. Uncertainties in the national CL calculations have been quantified (Hall et al., 2004b). However, due to the nature and scale of the underlying data, and the incomplete data for designated sites, there are additional uncertainties in using the national maps for site-specific assessments. With appropriate guidance the national soil CL map can be used as a first-level screening tool for assessing designated sites as demonstrated by the framework presented above. The CL “variance” map provides additional information at the national scale to help determine if soil acidity CL values extracted from the national map are appropriate, especially for small sites. For the larger or more complex sites it is even more important to gather information on the spatial location of the designated features and their relationships to habitat and soil types. The Endorsement Theory approach helps provide a further quality assurance measure of the appropriateness of CL values extracted from the national map and applied to designated species or habitats.

The practical hierarchy presented deals only with acidity; though a similar approach could be adopted for nitrogen. In a regulatory framework it is important that the uncertainties in the use of the national maps are fully understood and taken in to account. In an ideal world site-specific data would be collected for all sites of interest, and habitat- or species-specific dose–response relationships for acidity and nitrogen derived for all designated features. However, given the number of different designated habitats and species this would be an enormous, time-consuming and very costly task; and one no policymaker is likely to fund unless they could be certain at the outset that the results would be so very different from what can be obtained by using the national data to screen sites. The proposed hierarchy provides a practical series of steps to guide the policy-

maker in screening and assessing designated sites, using national maps where possible and appropriate, and providing additional tools to determine the robustness of the CL values used. It will also highlight where the national data are inappropriate and therefore where research and funding need to be focused.

Acknowledgements The authors gratefully acknowledge the UK Environment Agency for their contribution to the funding of this research. However, the views expressed are those of the authors.

References

- Calver, L. J., Cresser, M. S., & Smart, R. P. (2004). Tolerance of *Calluna vulgaris* and peatland plant communities to sulphuric acid deposition. *Chemistry and Ecology*, 20, 309–320.
- CLRTAP (1979). *Protocols to the convention on long-range transboundary air pollution*. Geneva, Switzerland: United Nations Economic Commission for Europe.
- Cohen, P. R. (1985). *Heuristic reasoning about uncertainty: An artificial intelligence approach*. Boston: Pitman.
- Dempster, A. P. (1967). Upper and lower probabilities induced by a multi-valued mapping. *Annals of Mathematical Statistics*, 38, 325–339.
- DETR (2000). *The air quality strategy for England, Scotland, Wales and Northern Ireland – Working together for clean air*. London, UK: Department of the Environment, Transport and the Regions.
- EU (1992). Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora. <http://europa.eu.int/comm/environment/nature>.
- Hall, J., Ulyett, J., Heywood, L., Broughton, R., Fawehinmi, J., & 31 UK experts (2003). Status of UK critical loads: Critical loads methods, data and maps. February 2003. Report to Defra (Contract EPG 1/3/185). <http://critloads.ceh.ac.uk>.
- Hall, J., Ulyett, J., Heywood, L., Broughton, R., & 12 UK experts (2004a). Update to: The status of UK critical loads – Critical loads methods, data and maps. February 2004. Report to Defra (Contract EPG 1/3/185). <http://critloads.ceh.ac.uk>.
- Hall, J., Ulyett, J., Heywood, L., Broughton, R., & Fawehinmi, J. (2004b). The National Critical Loads Mapping Programme Phase IV. Final report to Defra: July 2001–June 2004 (Contract EPG 1/3/185).
- Heywood, E., Skeffington, R., Whitehead, P., & Reynolds, B. (this issue). Comparison of critical load exceedance and their uncertainties based on national and site-specific inputs.
- Hornung, M., Bull, K. R., Cresser, M., Hall, J., Langan, S. J., Loveland, P. et al. (1995). An empirical map of critical loads for acidity in Great Britain. *Environmental Pollution*, 90, 301–310.
- Langan, S. J., Hall, J., Reynolds, B., Broadmeadow, M., Hornung, M., & Cresser, M. S. (2004). The development of an approach to assess critical loads of acidity for woodland habitats in Great Britain. *Hydrology and Earth System Sciences*, 8, 355–365.

- Loveland, P. J. (1991). The classification of the soils of England and Wales on the basis of mineralogy and weathering – The Skokloster approach. A report to the Department of the Environment under Research Contract Reference no. PECD 7/12/44.
- Rodwell, J. S. (Ed.) (1991). *British plant communities*, 5 volumes. Cambridge: Cambridge University Press.
- Shafer, G. (1976). *Mathematical theory of evidence*. Princeton, N. J., USA: Princeton University Press.
- Skeffington, R., Hall, J., Heywood, E., Wadsworth, R. A., Whitehead, P., Reynolds, B. et al. (2005). Uncertainty in critical load assessment models. Final report to the Environment Agency. R&D Project no. P4-120/4: Acidification and Annual Audits. December 2005. 152 pages.
- UBA (2004). Manual on methodologies and criteria for modelling and mapping critical loads & levels and air pollution effects, risks and trends. Texte 52/04 (ISSN 0722-186X), Umweltbundesamt, Berlin. <http://www.oekodata.com/icpmapping>.
- Wadsworth, R. A., & Hall, J. (this issue). Using endorsement theory and Dempster–Shafer formalism to reason with uncertain and incomplete information.