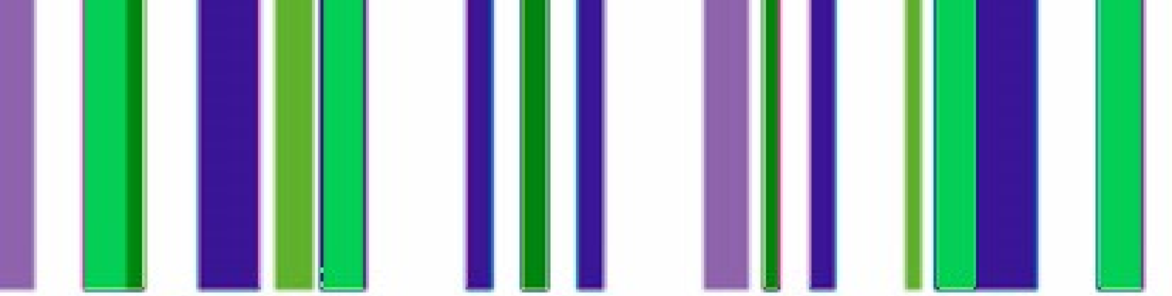

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Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology

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Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology

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PREFACE

The book contains the contributions at the NATO Study Institute on Exposure and Risk Assessment of Chemical Pollution – Contemporary Methodology, which took place in Sofia – Borovetz, Bulgaria, July 1–10, 2008.

Rapid advances in mathematics, computer science and molecular biology and chemistry have lead to the development in of a new branch of toxicology called Computational Toxicology. This emerging field is addressing the estimation and prediction of exposure risk and effects of chemicals based on experimental data, measured concentration and biological mechanisms and computational models of biological systems.

Mathematical models are also being used to predict the fate and transport of substances in the environment. Because this area is still in its infancy, there has been limited application from governmental agencies to regulating controllable processes, such as registration of new chemicals, determination of estimated exposure and risk based limits and maximum acceptable concentrations in different compartments of the environment – ambient air, waters, soil and food products. However, this is soon to change as the ability to collect, analyze and interpret the required information is becoming increasingly more efficient and cost effective. Full implementation of the new processes have to involve education on both part of the experimentalists who are generating the data and the models, and the risk assessors who will use them to better protect human health and the environment.

The Goal of the Advanced Study Institute was to evaluate existing knowledge and practical application of modern technologies for exposure and risk assessment of chemical environmental pollution with emphasis on methodologies and the models used for environmental security. Particular attention was paid to models useful for the quantitative and qualitative identification, estimation of exposure and risk. Research needs in this complex scientific field were identified and the strategy for prediction and prevention of chemical threats originating from intentional pollution were outlined. The ASI clearly contributes to exchange of experience between experienced scientists in this field and young researchers from NATO and Partner and Mediterranean Dialogue countries. We hope that this exchange will inevitably help the development of national policies, and the international collaboration for practical application in risk reduction in order to minimize the environmental pollution implication for the economic instability.

The *Main Objectives* of the Advanced Study Institute were:

- To perform a review of the computational modelling technology achievements for environmental fate, exposure, hazard, and risk assessment of chemical pollutants in air, water, soil and biota. To discuss the economic significance
- To estimate the screening level risk assessment modelling to assess and prioritize chemicals
- To evaluate the probabilistic risk assessment methods for intentional pollution to help the risk managers in uncontrollable processes
- To review the approaches for modelling of adverse health and environmental effects
- To perform comparative evaluation of currently used models on the criteria of sensitivity, variability and uncertainty
- To evaluate the additional criteria as predictive value, advantages, validations and limitations of models

In order to achieve the goals as stated above and to fulfill the main objectives, the scientific program included lectures in the morning sessions and demonstrations and exercises in the afternoons in small working groups, as well as round table and free discussions between scientists with different expertise to allow each young investigator to receive theoretical and practical knowledge sufficient to initiate the use of the new methodologies for evaluation of environmental security as related to exposure evaluation and risk assessment.

Conclusions were formulated based on the students' interim reports as well as on the results formulated by all participants at the final discussions session. Taking into account that the proposed objectives of the project were in principal to share information on risk assessment methods, to give information to the students and to share experience, the discussions remarked the following issues.

Scientific approach: The presentations on chemical exposure and risk assessment were helpful introductions to exposure and risk assessment concepts and models as was the lecture on risk assessment of chemical pollutants and mixtures in the environment. The scientific_program included very interesting lectures which were very well structured. The topics discussed covered all the main aspects of exposure and risk assessment of chemical pollution and modeling. The round table discussions and the working groups were a very good way to interact with the other participants, to share experience, opinions and to find solutions for specific problems (topics). The students learned about integrated approach of risk assessment in Europe, United States, North Africa and Canada, got general information on toxicology and information about the fate of pollutants in different fields and in different countries, learned about how to approach a risk situation and something new about pollution problems: traffic, industrial, agriculture, soil, water, underground water, air.

Practical Approach: For the students most interesting thing was to actually learn new models and put them into practice. This was in their opinion the most educative and interactive activity. The students learned a lot about measuring and modeling to assess the exposure and risks of chemicals in the environment. Exercises were performed in order to learn to work with new models software provided by the lecturers. Every student had a presentation about his work from different fields: chemistry, biology, environmental engineering, biotechnology, geography, public health, and during the Poster sessions there have been interesting discussions with other colleagues or lecturers. Representative case studies of each country regarding a specific problem and the associated solutions could start international collaboration for practical application in risk management in order to minimize the environmental pollution. The competition between groups on risk communication subject was helpful for students to better understanding the need of an appropriate risk communication as part of the risk assessment process and provided exchange of knowledge in different areas of expertise. In the competition, the students learned about how to act in the very future and how to manage with the power of decision.

Cultural Approach: Participating teams from many countries assured the socialization, communication and cultural exchange.

Recommendations based on the intermediate reports made by four groups of students as well as based on the final discussions session for recommendations were formulated as concerning the fields of:

Educational needs: Education is needed at all levels, from initial level (undergraduate, MSc and PhD students) as well as at for lifelong learners (academic staff, specialists, and professionals) having a particular role in the different stages of the risk assessment process: data providers, environmentalists, public health specialists, toxicologists, specialists in modeling, risk assessors. Some specific suggestions were formulated: a/ for the lectures content; b/ for the program organization; c/ for possible invited participants.

Research needs: Research priorities should be formulated adapted to the science development in this very specific domain. Research projects for risk assessment should have a multidisciplinary approach, combining the expertise from various specialties. Research is needed in a very large pallet of subjects, in order to develop new or improved methods for all stages of risk assessment activity. Some domains were identified to be well developed: a/ human health studies, environmental epidemiological studies; b/ new methodologies in risk assessment regarding nano-pollutants; c/ computational modeling technology application for environmental risk assessment; an efficient risk management model requires available information concerning the distribution of chemicals in the environment and the associated health impacts, which are centralized in databases of environmental monitoring as well as databases on human health monitoring; therefore models should be improved, in order to reduce their limitations: validation and uncertainty determination of the models.

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NEW VERSUS CLASSIC APPROACHES FOR CHEMICAL RISK ASSESSMENT AND MANAGEMENT

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Abstract. In recent years, the public has become increasingly aware of the presence of harmful chemicals in our environment. Many people express concerns about chemicals and other foreign substances in food, in drinking water, and toxic pollutants in the air. Exposure and risk assessment of chemical environmental pollution have been widely studied. Risk assessment provides a systematic approach for characterizing the nature and magnitude of risks associated with environmental health hazards. All activities, processes and products have some degree of risk. Particular attention will be given to models useful for the quantitative and qualitative identification, estimation of exposure and risk. This science is based on experimental data, measured concentration and biological mechanisms. Mathematical models have been used to estimate the concentrations of different substances in the environment. This justifies the need for development and studies on this field in the same interest as classic methodology. The ultimate aim of this chapter is to: (1) provide a basic explanation of risk assessment for people involved in environmental health issues; (2) evaluate existing knowledge and practical application of modern technologies for exposure and risk assessment of chemical environmental pollution with emphasis on methodologies, models used for the environmental security; (3) Review of computational modeling technology achievements for environmental fate, exposure and risk assessment of chemical pollutants in air, water, soil and biota; (4) Modeling of adverse health and environmental effects. In conclusion, Risk assessments can guide regulators in abating environmental hazards. Members of the public who learn the basics of risk assessment can improve their understanding of both real and perceived environmental hazards, and they can work more effectively with decision makers on solutions to environmental problems.

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1. Introduction

Chemicals in the environment can be either beneficial or harmful, depending on many factors, such as the amounts to which we are exposed. Low levels of some substances may be necessary for good health, but higher levels may be harmful. Health risk assessments are used to determine if a particular chemical poses a significant risk to human health and, if so, under what circumstances. Could exposure to a specific chemical cause significant health problem? If it were possible to prevent all human exposure to all hazardous chemicals, there would be no need for risk assessment. However, the total removal of harmful pollutants from the environment is often infeasible or impossible, and many naturally occurring substances also pose health risks. Risk assessment helps scientists and regulators identify serious health hazards and determine realistic goals for reducing exposure to toxics so that there is no significant health threat to the public.

The scientific application of risk assessment techniques to the hazard of chemicals in the environment is the subject matter of this chapter. The probability that any given level of a chemical in the environment present a hazard to the exposed populations whether humans, animals, fish or other species, can be extremely difficult to determine, but it is essential that rigorous scientific methods are used in any such assessment. Unfortunately, in many cases the available data are not good enough to make precise prediction possible.

As broadly defined, risk assessment can be used to predict the likelihood of many unwanted events, including industrial explosions, workplace injuries, failures of machine parts, natural catastrophes, injury or death from an array of voluntary activities, diseases, natural causes, life-style or others (Wilson and Crouch, 1987).

The traditional approach used to estimate risks from chemical agents is to assume that the observed dose–response relationship is the same from one set of circumstances to the other, providing that important determinants (e.g. mechanisms) have an equivalent effect on the dose–response relationship. Health risk assessment however is a separate and distinct discipline which uses toxicology data collected from animal studies and human epidemiology, combined with information about the degree of exposure, to quantitatively predict the likelihood that a particular adverse response will be seen in a specific human population (NAS, 1994).

Since 1980, many environmental regulations and some occupational health standards have, at least in part, been based on the results of low-dose extrapolation models and exposure assessments (Preuss and Ehrlich, 1987). For example, risk-assessment methodologies have been used to set standards for pesticide residues, food additives, pharmaceutical agents, drinking water, soil and ambient air, as well as exposure limits for contaminants found in indoor air, consumer products and other media (Paustenbach, 1989).

Risk assessment has been separated into four sub disciplines: hazard identification, dose–response assessment, exposure assessment and risk characterization (NAS, 1994). This has been called the "risk assessment paradigm." Hazard identification is the first and most easily recognized step in risk assessment. It is the process of determining whether exposure to an agent could (at any dose) cause an increase in the incidence of adverse health effects in humans or wildlife. Dose–response evaluations define the relationship between the dose of an agent and the probability of a specific adverse effect in laboratory animals. Exposure assessment quantifies the uptake of toxic chemicals from the environment by any combination of oral, inhalation and dermal routes of exposure. The most important part of an assessment, risk characterization, summarizes and interprets the information collected from previous activities and identifies the limitations and the uncertainties in risk estimates (Preuss and Ehrlich, 1987).

2. Concepts of Exposure, Intake, Uptake, and Dose

Exposure assessment is the most problematic area in the risk assessment process for environmental pollutants and is the source of most of the uncertainty in the estimation of risk. When assessing the exposure of chemical to the environment the life cycle of a substance should be considered. The previous release of chemicals is also need to be taken into account. These releases may have an accumulative effect that gives rise to a "background" concentration in the environment. There are two major processes by which a chemical can cross the boundary from outside to inside the body. Intake involves physically moving the chemical in question through an opining in the outer boundary (usually the mouth or nose), a medium such as air, food, or water; the estimate of how much of the chemical enters into the body focuses on how much of the carrier medium enters and described as chemical intake rate. The resulting estimated intake by the average individual is then usually compared with intake criteria, such as ADI or TDI (acceptable and tolerable daily intake, respectively) (Birmingham et al., 1989; Furst et al., 1990). The second process by which a chemical can cross the boundary from outside to inside the body is uptake. Uptake involves absorption of the chemical through the skin or other exposed tissue such as the eye (EPA, 1992).

Exposure-related models can be thought of as falling into two broad categories as shown in Figure 1.

1. Concentration models, which predict concentrations in environmental media (e.g. air, water, food, soil) in units of mass per unit volume and
2. Contact models, which predict exposure in units of concentration per unit time although concentration models do not truly estimate exposures, output from such models is often combined with data on human time-activity patterns to produce exposure estimates (NRC, 1991)

Concentration models typically incorporate information about important fate (e.g. particle settling), transport (e.g. meteorological dispersion) and transformation (e.g. photochemical reactions) mechanisms to predict environmental concentrations. Similarly, to estimate exposures, contact models incorporate knowledge of exposure-related determinants (which are analogous to concentration-related mechanisms), such as lifestyle characteristics (e.g. tobacco and alcohol use) and time-activity patterns (e.g. time spent exercising outside the residence). Mechanistically based research to improve these models is a potentially useful approach to reducing exposure-related uncertainty. Particularly useful would be development of "integrated human exposure models" that allow for realistic comparisons of exposures across pathways (e.g. inhalation in the workplace versus ingestion through the diet), across agents and agent classes (e.g. pesticides versus heavy metals) and across populations (e.g. urban versus rural).

To make quantitative risk estimates, assessors essentially take what is known about the environmental health paradigm and critical underlying mechanisms make necessary science policy decisions according to agency guidelines and work through the four major steps in risk assessment (Figure 2). During this process, they are frequently confronted with the need to extrapolate data from experimental conditions to real-world situations or from one real-world situation to another.

2.1. APPROACHES TO QUANTIFICATION OF EXPOSURE

Although exposure assessments are done for a variety of reasons, the quantitative exposure estimate can be approached from three different ways.

1. The exposure can be measured at the point of contact (the outer boundary of the body) while it is taking place, measuring both exposure concentration and time of contact and integrating them (point-of-contact measurement).

2. The exposure can be estimated by separately evaluating the exposure concentration and the time of contact, then combining this information (scenario evaluation).
3. The exposure can be estimated from dose, which in turn can be reconstructed through exposure has taken place (reconstruction).

These three approaches to quantification of exposure (or dose) are independent, as each is based on different data. The independence of the three methods is a useful concept in verifying or validating results. Each of the three has strengths and weaknesses; using them in combination can considerably strengthen the credibility of an exposure or risk assessment.

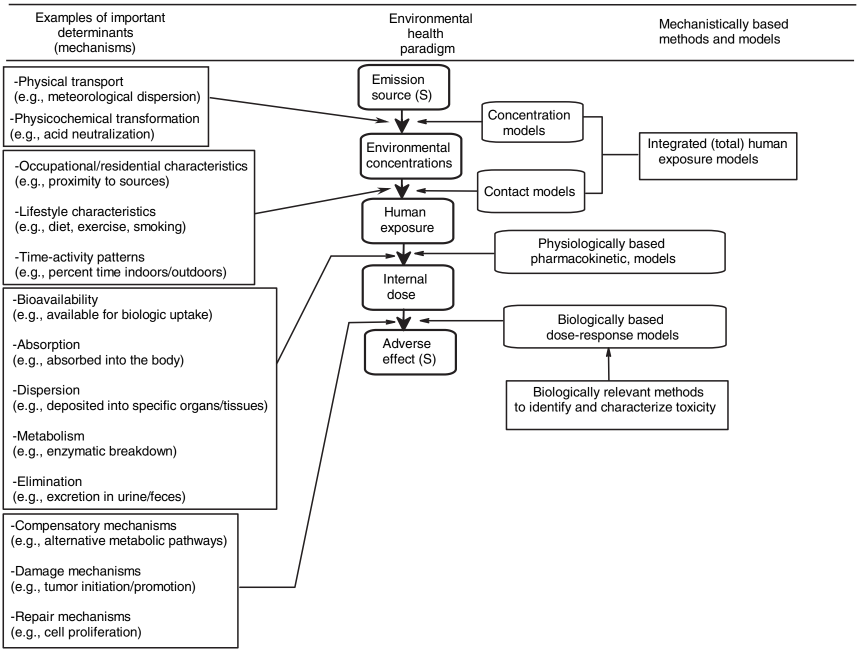

Figure 1. Important mechanistic determinants of events in an environmental health paradigm and their relationship to mechanistically based methods and models.

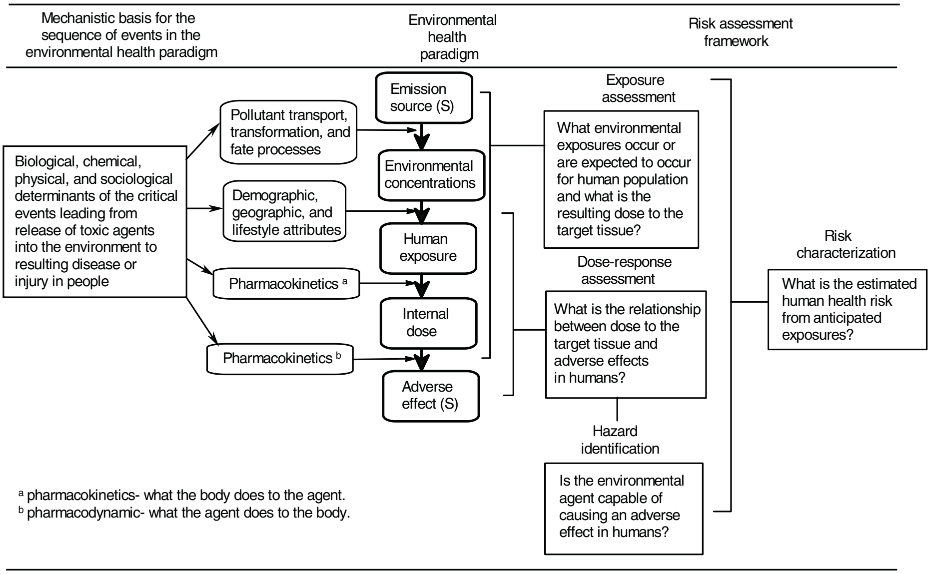

Figure 2. The mechanistic basis for an environmental health paradigm and its relationship to the risk assessment framework.

2.2. RELATIONSHIPS OF EXPOSURE AND DOSE TO RISK

Both exposure and dose are often combined with exposure–response or dose–response relationships to estimates risk, the probability of an adverse effect occurring. There are a variety of risk models, with various mathematical relationships between risk and dose or (less frequently) exposure. A major function of the exposure assessment as part of a risk assessment is to provide the exposure or dose values, and their interpretations.

There are several definitions for risk, but all have as a common theme, the fact that risk is a combination of the undesirable consequences of accident scenarios and the probability of these scenarios. The concept of risk includes both undesirable consequences, e.g., the number of people harmed, and the probability of occurrence of this harm. Sometimes, risk is defined as the expected value of these consequences.

The exposure and dose information available will often allow estimates of individual risk or population risk, or both. Presentation of risks in a risk assessment involves more than merely a numerical value, however. Risks can be described or characterized in a number of different ways.

3. Risk Assessment Approach

One approach that EPA uses to evaluate and compare the health risks of systemic toxicants is calculation of either the dose (i.e. reference dose – RfD) (EPA, 1987) or the exposure concentration (i.e. reference concentration – RfC) (EPA, 1990) that represents an insignificant risk to human health over a life. The RfC and RfD are point estimates of a "safe" level for an environmental agent, below which there will be no adverse effects on health. They provide no information about the associated dose–response relationship and, therefore, do not allow for quantitative risk assessment. The RfC and RfD are calculated by taking either the lowest observed adverse effect level (LOAEL) or the no observed adverse effect level (NOAEL) from animal studies (or human studies, if available) and, based on professional judgment about the adequacy of the data, dividing by a series of uncertainty factors (EPA, 1987, 1990).

3.1. INDIVIDUAL RISK

Individual risk is risk borne by individual persons within a population. Risk assessments almost always deal with more than a single individual. Frequently, individual risks are calculated for some or all of the persons in the population being studied, and are then put into the context of where they fall in the distribution of risks for the entire population. Descriptions of individual risk can take various forms, depending on the questions being addressed. For the risk manager, there are often key questions in mapping out a strategy for dealing with individual risk either cancer or non-cancer. Individuals at the high end of the risk distribution are often of interest to risk managers when considering various actions to mitigate risk.

3.2. POPULATION RISK

Population risk refers to an estimate of the extent of harm for the population or population segment being addressed. Risk managers may need questions addressed such as the following:

- How many cases of a particular health effect might be probabilistically estimated for a population of interest during a specified time period?
- For non-carcinogens, what portion of the population exceeds the reference dose (RfD), the reference concentration (RfC), or other health concern level?
- For carcinogens, how many persons are above a certain risk level such as 10^{-6} or a series of risk levels such as 10^{-5}, 10^{-4}, etc.?

- How do various subgroups fall within the distributions of exposure, dose, and risk?
- What is the risk for a particular population segment?

4. Uses of Risk Assessment

Not only are risk assessments done for a variety of purposes, but the toxic endpoints being assessed (e.g., cancer, reproductive effects, neurotoxic effects) can also vary widely. Endpoint and other aspects of the hazard identification and dose–response relationships can have a major effect on how the exposure information must be collected and analyzed for a risk assessment.

Risk assessments can also guide regulators in abating environmental hazards. Members of the public who learn the basics of risk assessment can improve their understanding of both real and perceived environmental hazards, and they can work more effectively with decision makers on solutions to environmental problems.

5. Risk Estimates, Approaches, Advantages and Pitfalls

5.1. POINT AND PROBABILISTIC RISK ESTIMATES

To date, almost all human health risk assessments have used conservative "point" estimates (i.e., Probabilistic risk assessments are enjoying increasing popularity as a tool to characterize the health hazards associated with exposure to chemicals in the environment. Because probabilistic analyses provide much more information to the risk manager than standard "point" risk estimates, this approach has generally been heralded as one which could significantly improve the conduct of health risk assessment. The primary obstacles to replacing point estimates with probabilistic techniques include a general lack of familiarity with the approach and a lack of regulatory policy and guidance (Finkel, 1990a; Burmaster and Lehr, 1991; McKone and Bogen, 1991). The "probabilistic" risk assessment approach uses a distribution of data rather than a single data point to represent key exposure variables (chemical, concentrations, frequency, and duration of contact, body weight, etc.). It has also been suggested that the probabilistic analyses offer a more accurate estimate of the plausible risk, especially at "upper-bound" exposures (between 95th and 99th percentile) (Burmaster and Lehr, 1991). Although probabilistic analyses were rarely used in health risk assessment prior to 1989, over the past 10 years a number of assessments have been conducted using this approach.

5.2. ADVANTAGES VERSUS PITFALLS OF THE POINT ESTIMATE APPROACH

Some of the relative advantages and disadvantages of the point estimates vs. the probabilistic analysis are presented in Table 1. One obvious advantage of the point estimate approach is that calculation of the health risk estimate is relatively straightforward and requires little, if any, knowledge of the scientific underpinnings of the various exposure factors. Indeed, all that is required is a calculator and patience. A second advantage, and often the most important one, is that it is readily accepted by state and federal regulatory agencies.

The limitations of the point estimate approach are numerous. A major shortcoming lies in the fact that repeated use of upper-bound point estimates, as is recommended by the USEPA to calculate a reasonable maximal exposure (RME), typically leads to unrealistic estimates of health risk and unreasonable clean-up goals (Burmaster and Lehr, 1991; Burmaster and Hattis, 1993).

In summary, the RME, although perhaps more reasonable and useful than the worst-case “maximally exposed individual” (MEI), still fails to realistically estimate potential upper-bound exposures for the vast majority of the general population. Perhaps the major shortcoming inherent in the point estimate approach is that it provides a limited amount of useful information to the risk manager and the public.

The point estimate is not completely without merit Table 1. It is most useful as a screening approach which approximates a remote, yet plausible, worst-case situation for some subpopulations of potentially exposed persons (sometimes referred to as a “bounding estimate”). If the potential health risks estimated by such a conservative approach are negligible, then more complex evaluations need not be conducted.

5.3. ADVANTAGES VERSUS PITFALLS OF THE PROBABILISTIC ANALYSIS

The probabilistic analysis addresses the main deficiencies of the point estimate approach because it imparts a great deal more information to the risk manager. Instead of presenting a single point estimate of risk, it characterizes a range of potential risks and their likelihood of occurrence. In addition, those factors which most affect the results can be easily identified (NRC, 1991; Sexton et al., 1993; NAS, 1994).

5.4. APPLICATIONS OF THE PROBABILISTIC APPROACH

As presented in Table 2, we believe that virtually all current applications of human and environmental health risk assessment, including the setting of occupational and environmental health standards and dose–response criteria, could benefit from incorporation of population distributions (NRC, 1991; Sexton et al., 1993; NAS, 1994).

TABLE 1. Advantages and disadvantages of using the point estimate or the probabilistic approach in health risk assessments.

Advantages	Disadvantages
Point estimates:	
Simple, accessible	Repeated use of conservative point estimates
Readily accepted by regulators	Provides limited information for risk managers and public
Can provide a bounding estimate	No associated measure of confidence
	Sensitivity or uncertainty analyses usually not very meaningful
Probabilistic assessment:	
Provides more meaningful information to risk manager and public	More complicated and, therefore, more time-consuming
Avoids disputes over best point estimate	More difficult to conduct quality assurance of the calculations
Risk estimates are associated with a quantitative measure of uncertainty	Current regulatory guidelines do not encourage its use
Eliminates creeping conservatism	Can fail to account for interdependent variables
Allows for quantitative evaluation of conservatism in point estimate (RME) approach	
Sensitivity analysis more meaningful	

6. Risk Management

One of the most difficult questions of risk management is: how much risk is acceptable? While it would be ideal to completely eliminate all exposure to hazardous chemicals, it is usually not possible or feasible to remove all traces of a chemical once it has been released into the environment. US EPA uses the following guidelines regarding acceptable risk: For carcinogenic effects a lifetime cancer risk of less than 1E-4 for the most exposed person and a lifetime cancer risk of less than 1E-6 for the average person as a result of exposure to the potential carcinogen from all significant exposure pathways for a given medium (Wilson and Crouch, 2001). For noncarcinogenic effects a concentration is calculated that the corresponds to an HI of 1, which is the level of exposure pathways in a given medium below which it is unlikely for even sensitive populations to experience adverse health effects.

TABLE 2. Applications of the probabilistic risk assessment and some recommended methodologies.

Application	Suggestion
Superfund risk assessments	Use "reasonable maximal exposure" (RME) as a screening method, then probabilistic methods for detailed estimate of risk, if warranted
Setting occupational environmental, and consumer standards (TLVs, MCLs, and ADIs)	Assess degree of conservatism in existing or proposed standards using probabilistic vs. point estimate evaluation
Setting health-based cleanup levels for soils	Replace the point estimate approach with a probabilistic analysis; select the appropriate percentile of the cleanup level
Setting toxicity criteria such as reference doses and cancer potency factors	Use a weight – of-evidence approach to assess all the available data and define the toxicity value as a specified confidence limit
Reality check of USEPA default values	Assess degree of conservatism in current default values with a probabilistic evaluation
Air toxics risk assessments	Replace "most exposed actual person" as required in the clean air act and some state agencies with a probabilistic assessment of residual risk for the 50th, 90th, or 95th percentile person

Risk management involves weighing policy options and selecting an appropriate course of action by integrating the results of risk assessment with engineering data (e.g. control feasibility), social concerns (e.g. who benefits versus who pays), economics issues (e.g. cost-effectiveness) and political realities (e.g. special interests); these decisions are termed "risk management policy". Another way to visualize the risk assessment paradigm is shown in Figure 3 where the three phases of decision making exist as overlapping spheres and together from a series of feedback loops. In this schema, the information and understanding generated by the research program directly improve the scientific basis for decisions about risks and the information needs, identified as part of risk assessment and risk management, influence the direction and nature of supporting research (Sexton et al., 1993).

Risk management activities as follows:

- **Identify**. State the risk in terms of condition(s) and consequence(s); capture the context of the risk; e.g., what, when, where, how, and why.

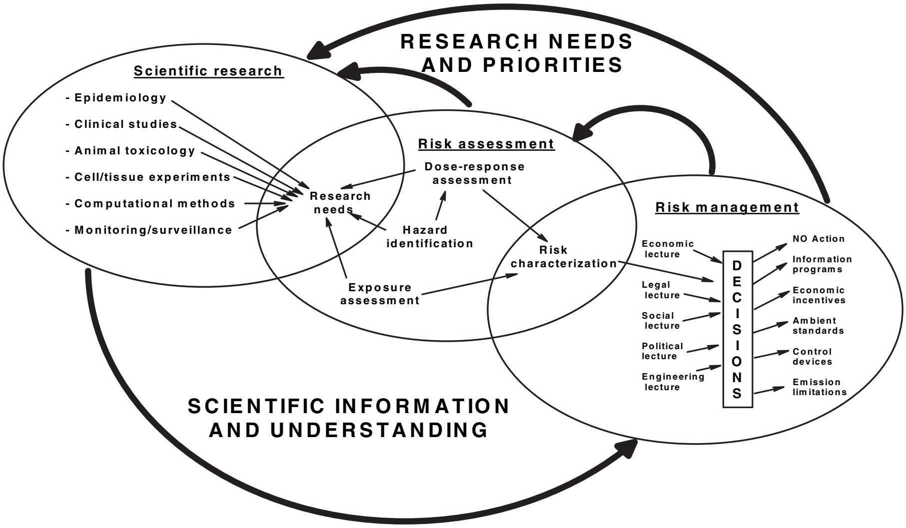

Figure 3. Risk assessment and management paradigm. (Sexton et al., 1993.)

- **Analyze**. Evaluate probability, impact/severity, and time frame (when action needs to be taken); classify/group with similar/related risks; and prioritize. Methods such as PRA are used to analyze risk from rare events quantitatively.
- **Plan**. Assign responsibility, determine risk approach (research, accept, mitigate, or monitor); if risk will be mitigated, define mitigation level (e.g., action item list or more detailed task plan) and goal, and include budget estimates.
- **Track**. Acquire/update, compile, analyze, and organize risk data; report results; and verify and validate mitigation actions.
- **Control**. Analyze results, decide how to proceed (re-plan, close the risk, invoke contingency plans, and continue tracking); execute the control decisions.
- **Communicate and document**. Essential risk status is to be communicated on a regular basis to the entire team. A system for documentation and tracking of risk decisions will be implemented.

7. The Debate About Risk Assessment

Criticism falls generally into three broad categories:

1. Existing scientific knowledge and understanding are insufficient or inappropriate to allow for meaningful quantitative estimates of risk (Weinberg, 1985; Foster et al., 1993).

2. Risk estimates are based on faulty or incomplete models, which rely on overly conservative default assumptions, causing estimated risks to be unrealistically high (Nichols and Zeckhauser, 1986; Ames and Gold, 1991; Whelan, 1993; Abelson, 1994a, b).
3. Scientific uncertainties associated with risk estimates are not adequately identified, characterized or communicated (Hattis and Kennedy, 1986; Bogen, 1990; Finkel, 1990b; Morgan and Henrion, 1992; NAS, 1994).

Although the debate about specific risk assessments is sometimes contentious, there seems to be general agreement on the necessity for risk assessment to be conducted in some form and on the value of the current system as a framework for organizing and analyzing the available scientific information. A consensus also seems to exist that targeted research to reduce critical scientific uncertainties is the key to making risk assessments more informed and more credible.

8. Conclusions

In conclusion, from chemical risk assessment the following remarks can be outlined:

1. A quantitative estimate of risk was obtained.
2. Potential risk reduction measures were identified.
3. The potential benefits of these prevention measures were quantified.

If trustworthy, these results are clearly of significant use to a decision maker. What is required for these results to be trustworthy? First, the scenario set must be substantially complete. If dominant scenarios are not identified, then the overall frequency result is in error. Moreover, if these unidentified scenarios have ingredients not present in the scenarios that are identified, then potentially useful prevention measures are not identifiable from the results.

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DOSE RESPONSE EXTRAPOLATION FOR ACUTE EFFECTS OF TOXIC AGENTS AND ITS RELEVANCE TO PREDICT HEALTH RISK RELATED TO DISASTER AND TERRORISM ASSOCIATED EVENTS

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Abstract. Acute exposure to chemical agents can occur as a result of industrial or transportation accidents, fires, natural disasters, or terrorist acts, and may affect both occupational and residential populations. Exposure time and dose are both critical determinants of health risk in such situations. Yet the effects of differing exposure duration along with differing concentration are seldom systematically examined in standard acute toxicology studies. A key consideration for assessing acute exposure risks is how toxicological modes of action (MOA) differ between the acute and chronic exposure situation. Many MOA of concern for chronic exposure will not be relevant for the acute exposure situation. It is also important to understand acute dosimetry and the conditions under which algebraic approaches such as Haber's rule (concentration × time = constant) will serve as an appropriate tool for dose extrapolation. Our analysis shows that Haber's rule is only relevant in the initial stages of exposure, where the relationship between internal dose and time is linear. At later stages of exposure when the internal dose approaches steady state conditions, Haber's rule will be an inappropriate basis for dose-extrapolation. This may be a particular problem for chemicals which approach steady state conditions soon after the start of exposure. One alternative for conducting acute exposure extrapolations is physiologically-based toxicokinetic modeling. As illustrated with an example involving acute exposure to fire retardants, this type of modeling has the potential to generate biologically-informed extrapolations of target organ doses for various exposure points.

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1. Introduction

Acute exposures were of considerable interest in the field of toxicology from the 1930s to 1960s when the immediate effects of chemical exposures (e.g., in occupational settings) were of great interest. Although the chronic toxicity of some chemicals (e.g., benzene, aniline dyes) was well established in this time period, for many chemicals the available toxicological data were limited to those obtained from acute lethality studies (Patty et al., 1930; Waite et al., 1930; Nuckolls, 1933). With the subsequent recognition that many organic chemicals posed chronic health hazards, as well as the major expansion in chronic animal testing starting in the late 1960s, acute toxicity became a lesser concern. This trend has now been altered. Owing to concerns about disaster- and terrorism-related exposures, government agencies have given increased attention to understanding the mechanisms of acute toxicity in order to establish safe levels for different types of acute chemical exposures (e.g., accidental versus intentional, occupational versus residential) (U.S. EPA, 2004). Because exposure conditions will vary from situation to situation (e.g., in terms of timeframe, population of interest), and different risk-management applications require differing levels of conservatism, a variety of acute exposure limits have been, and will continue to be, generated including short term occupational exposure limits (STELs), Acute Exposure Guidelines (AEGLs), Emergency Response Planning Guidelines (ERPGs), Minimum Risk Levels (MRLs), and Acute Reference Exposures (AREs) (Woodall, 2005). These efforts require coordination and a common understanding of the issues related to evaluating the risks of acute toxicity (Rhomberg and Lewandowski, 2005). Below, we discuss some of these issues in an effort to highlight some of the differences between risk assessment for chronic and acute effects and identify data gaps where additional research might improve the available methods.

2. Toxicological Modes of Action

A key element in conducting risk assessment for acute exposures is to understand how such exposures are fundamentally different from chronic exposures. A key concept for developing this understanding is that of the toxicological Mode of Action (MOA) (Anderson and Dennison, 2001; Butterworth et al., 1995; Bogdanffy and Jarabek, 1995). The MOA describes how, on a fundamental level, a chemical causes harm to the body. Typical toxicological MOAs include inflammation, induction of apoptosis (programmed cell death), direct DNA damage (e.g., adduct formation), or inhibition of critical enzymes. The *mode* of action should be distinguished from the *mechanism* of action. Whereas the mode of action describes a generic process that is likely to be relevant for a range of compounds, the mechanism of action is likely to be a more narrowly defined idea and may be relevant to only a single chemical (e.g., "irreversibly binding a certain enzyme at a particular amino acid residue"). Understanding the MOA enhances our ability to predict potential human health risks because knowledge of the MOA allows one to account for species-specific differences in metabolism, the existence of an effect threshold, or effects on particularly sensitive subgroups in the human population such as children or the elderly (Anderson and Dennison, 2001; Bogdanffy and Jarabek, 1995).

Not all toxicological MOA are relevant for acute exposure situations. Because acute toxicity is, by definition, a process that occurs over a very limited period of time, modes of action that involve a sustained biological response (e.g., induction of cell proliferation) will not be relevant for the acute scenario. Conversely, those MOA involving rapidly occurring processes that quickly result in system failure will be of greatest concern for acute exposures. The following MOA can be expected to be relevant to the acute exposure situation:

- **Direct destruction of cells/tissues**. The simplest mode of action, this involves direct chemical attack on tissue components and is the mode of action involved with caustics (e.g., acids, bases, hexavalent chromium), lipid solubilizing compounds (e.g., solvents, detergents) and highly reactive and soluble gases. Since the effect of such chemicals is essentially immediate and is greatest where concentrations are at their maximum, these effects are most significant at the portals of entry (e.g., the nasal mucosa, the lung alveoli) and are substantially, if not totally, attenuated beyond these sites. Physiological mechanisms (airway constriction, changes in breathing patterns, mucous membranes) are present to limit the entry of these types of chemicals into the systemic circulation. It is possible, however, that at sufficiently high concentrations, there may be sufficient penetration or absorption such that systemic effects could occur.

- **Binding/Inactivation of critical cellular components**. This mode of action involves not complete destruction of cellular components but their alteration or inactivation. Protein cross linkers (e.g., formaldehyde), alkylating agents, and redox cyclers (quinones) all may cause acute toxicity by disrupting the function of molecules needed for cellular metabolism, cell structure and integrity, or maintenance of other cellular components. Again, owing to the reactivity of these compounds, their effects will be localized to the portal of entry, except at exceptionally high concentrations or where metabolism generates the ultimate toxicant (discussed below).

- **Inflammation**. Few toxicants cause inflammation directly (i.e., by directly stimulating release of inflammatory molecules); for most chemicals, inflammation is a secondary effect produced by direct destruction of target cells, tissues, and molecules. Thus, most inflammation occurs as a downstream response to the two modes of action described above. Cases where inflammation is the proximate effect would include toxicologic responses to particles, both inert (e.g., particulate matter) and allergenic (e.g., bacteria endotoxins), and responses to metals associated with fume fever, which appears to be mediated by direct release of immune modulators. Although inflammation may be seen as an appropriate biological defense mechanism, if sufficiently severe it may also lead to significant damage to the organism (deficits in physiological function, cardiovascular complications, etc.).

- **Interference with critical transport proteins**. Classic examples include those chemicals that interfere with the oxygen-binding ability of hemoglobin (e.g., carbon monoxide, nitrate).

- **Interference with cellular energy production**. This mode of action includes chemicals that interfere with energy production by the cell, by interfering either directly with oxidative phosphorylation (e.g., cyanide, hydrogen sulfide) or by disrupting mitochondrial integrity (e.g., pentachlorophenol). For this mode, it is the depletion of ATP (adenosine triphosphate), the energy currency of cells, that leads to toxicity through the failure of physiological processes that depend on ATP for needed energy.

- **Chemicals with toxic metabolites**. Toxicants of this type may be similar to the two modes listed above but are distinguished by a need for additional metabolism prior exerting toxic action. For example, the ocular toxicity associated with methanol involves conversion of methanol to formic acid (via formaldehyde), which results in a metabolic acidosis. Species differences in ocular metabolism of formic acid (e.g., rats vs. human) are known to correlate with susceptibility to toxicity.

- **Neurological depression**. Although the mechanism by which chemicals, particularly organic solvents, cause neurological depression (e.g., narcosis, dizziness) is not clearly understood, it appears to be related to solubilization of membrane lipids involved in insulating nerve fibers and facilitating nerve impulse transduction.

- **Neurotransmitter interference**. Distinct from generalized neurological depression, many insecticides are designed to cause rapid disruption of the acetylcholine neurotransmitter pathway (e.g., organophosphates, carbamates) or sodium channels important in nerve conduction (e.g., pyrethroids, DDT).

There are two other possible modes of action which may be important for acute exposures: allergic sensitization and reproductive/developmental effects. Regarding sensitization, the symptoms will likely occur outside of a 24–48 h window. Nonetheless, the exposure that renders the individual susceptible to reaction on further exposure is an acute phenomenon. Once the individual has been exposed to a sufficiently high dose of the sensitizer (e.g., diisocyanates, nickel) the process of immunological sensitization is set in motion. This "all or none" aspect of sensitization helps to distinguish it from truly chronic processes such as carcinogenesis where continued exposure (i.e., promotion) is required for tumor formation.

Toxicologists typically think of reproductive and developmental toxicity as something outside of the acute/subchronic/chronic scheme. This is perhaps in part due to the fact that testing for these endpoints is conducted separately from the standard toxicity testing program (i.e., 14-day, 28-day, 90-day and 2-year studies). In the last few decades however, toxicologists have become increasingly aware of "critical windows" in development (Rodier, 1994; Rice and Barone, 2000) which result in short periods of susceptibility to toxicological agents (reckoned in terms of days or hours). Acute exposure may result in damage to germ cells that can have adverse consequences in offspring. Similarly, exposure to developmental toxicants during early stages of cellular proliferation may have significant implications, even if the exposure is very brief.

In contrast to the above, modes of action which may reasonably be restricted to consideration of chronic exposure scenarios include the following:

- Carcinogenesis
- Immune system depression
- Enzyme induction
- Fibrosis (e.g., asbestosis, silicosis, cirrhosis)
- Delayed neuropathies (e.g., OPIDN, "dying back" axonopathies)
- Neuronal destruction (e.g., manganism, mercury poisoning)
- Disruption of homeostatic processes (e.g., erythropoiesis, thyroid hormone economy)

Many of these chronic effects clearly require a time component for damage to be fixed and/or accumulate before they produce functional deficits. Proliferative diseases (e.g., asbestosis, sarcoidosis, cirhossis, etc.) clearly fall into this category. However, the distinction between the acute and subchronic/chronic aspects of toxicity is not always so easy. For example, for chemicals where the mode of action involves generation of oxygen species that can react with critical macromolecules (e.g., chemicals generated by redox cyclers such as MPTP, acetaminophen, and paraquat) and depletion of antioxidant reserves, the damage may be manifested as a result of either acute or chronic exposures, depending on whether the dose rate is sufficient to overwhelm available reserves of antioxidants within an acute timeframe.

As noted previously, carcinogenesis is an unusual mode of action because it contains an initiating event (DNA mutation) which is acute in nature but the disease process itself is chronic and may involve a latency period spanning decades. Although regulators espouse the idea of a single molecule of exposure being associated with a defined risk, increased carcinogenic risk has not commonly been considered a concern for acute exposures.

A final note about MOA; it is often the case that chemicals may have one primary MOA of concern for acute exposures and a different MOA of concern for sub-chronic/chronic situations. A good example of this possibility is benzene, where the primary acute concern is narcosis, but the concern for longer-term exposure involves effects on hematopoiesis (i.e., anemia and leukemia). It also should be noted that some MOA that are relevant for acute exposures (e.g., inflammation) may also be causally connected to chronic sequellae (e.g., fibrosis, cirrhosis), whereas others (e.g., oxidation of the heme iron in hemoglobin) may not be associated with any chronic symptoms, particularly if treatment is rapid. Thus, an understanding of a chemical’s range of potential toxicological effects is necessary in order to use the concept of MOA in risk assessment.

3. Acute Dosimetry

As noted previously, regulators would ideally like to have the ability to identify safe acute exposure levels for a range of exposure durations in order to be able to confidently address different situations. In order to achieve this aim it is necessary to employ acute dosimetry. For example, if we have data from a controlled human exposure indicating a No Observed Effect Level for a chemical at 500 ppm for 10 min, it may be desirable to extrapolate that concentration to several different time frames, ranging from 30 min to 8 h. It would be imprudent to assume that the same concentration that produced no adverse effect with 10 min of exposure may also be tolerated for several hours; some adjustment is required, but to what extent?

One common approach for establishing equivalent exposure-effect concentrations involves application of Haber’s rule. Attributed to the German scientist Fritz Haber, who published an evaluation of acute animal exposures to nerve agents in 1924 (Haber, 1924), Haber’s rule states that, in terms of toxicological effects:

$$\text{Concentration} \times \text{Time} = \text{Constant}$$

That is, long duration exposures to low concentrations will result in the same effect (in terms of severity or percentage of the population affected) as shorter duration exposures at higher concentrations. The magnitude of the constant determines the intercept of the concentration-time curve, which will have a slope of −1 on a log-log plot of equally toxic combinations of air concentration and duration (Figure 1). Using Haber's rule one can in theory mathematically adjust exposure concentrations for the any duration. Thus if we have a no effect level for 15 min of exposure at 20 ppm (C × T = 20 ppm × 0.25 h = 5 ppm-h), an equivalent effect would be expected if the exposure lasts for 2 h at 2.5 ppm (2.5 ppm × 2 h = 5 ppm-h). A critical assumption required in the use of Haber's rule is that the adverse effects (and the MOA that produces them) are the same over time frame of interest. Thus, the approach would not be valid for extrapolating an acute exposure based on anesthesia to a subacute exposure where hematological effects are a greater concern.

While some evaluations have demonstrated the accuracy of Haber's rule (also called Haber's Law) as long as the types of chemicals involved are narrowly constrained and the timeframes over which extrapolation is conducted are not excessive, others have reported significant deviations (discussed in Rozman, 2000). The robustness of applying Haber's rule for health risk assessment has been questioned in part due to these exceptions (Atherley, 1985).

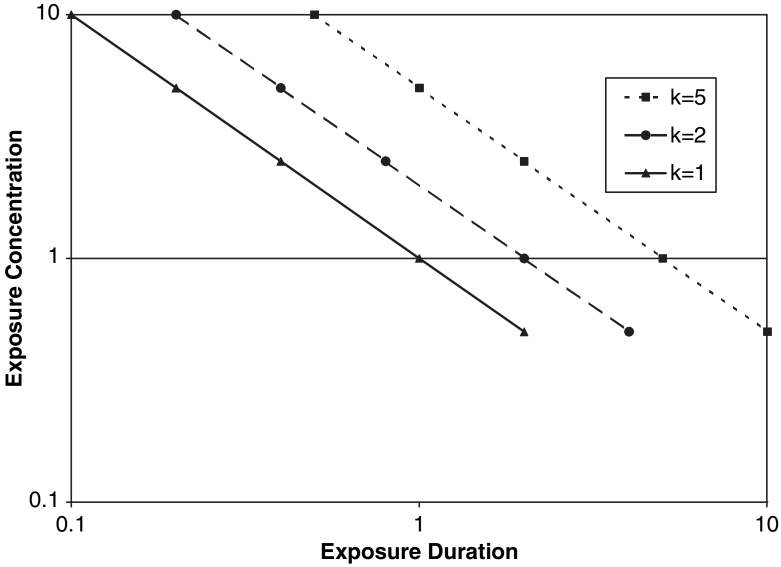

Figure 1. Effect of different values of k on the concentration – time relationship described by Haber's rule.

Interestingly, Rozman (2000) and Rozman and Doull (2001) have suggested that the reported deviations may be due to inherent differences in the experimental data being compared (owing to study design issues), rather than to a true deviation from C × T = constant. Other attempts at using Haber's rule as a general dosimetric approach have focused on defining a broader form which raises either the air concentration or the time to a power (e.g., $C^x \times T = k$) (for example, Ten Berge et al., 1986; Ten Berge and Stallen, 1995). The powers can be estimated empirically if one has data on a sufficient number of alternative C and T combinations.

Just as it may be inappropriate to assume that Haber's rule applies to all chemicals, it also appears inappropriate to assume that it applies to all phases of exposure. This can be illustrated by simple toxicokinetic modeling. Let us take as an example a chemical with very simple kinetics: the body can be described

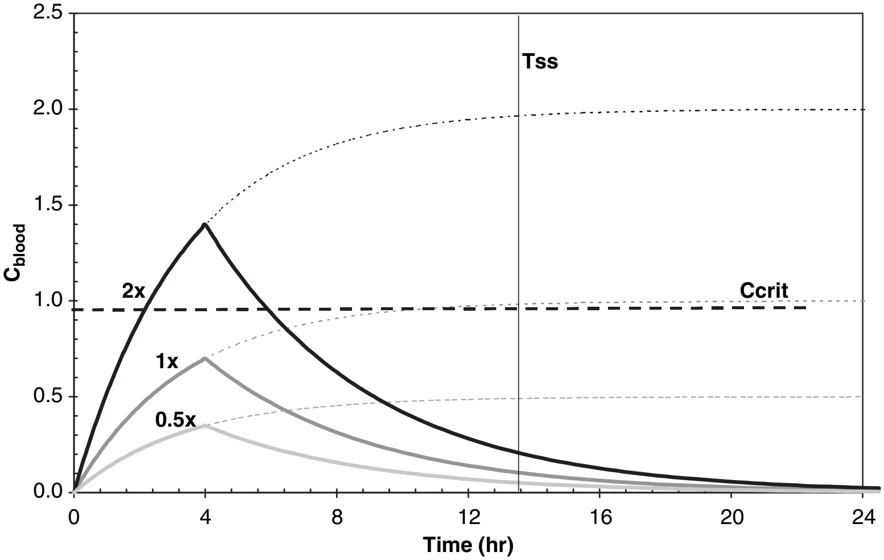

Figure 2. Blood concentration vs time for an example inhaled toxicant. Both uptake and elimination are modeled as first order processes. Exposure starts at time zero and ends after 4 h, at which point blood concentrations of the chemical begin to decline. The thick line indicates the actual blood concentration while the thin line indicates what would be expected if exposure had continued. The figure also shows the effect of changing exposure concentration (C) on the toxicokinetic profile. Note that changing the exposure concentration does not affect the time required to reach steady state and that the blood concentration at study state depends entirely on the exposure concentration. The time to reach a critical value, which could reflect an adverse effect threshold, does vary with changes in concentration, being reached more quickly as exposure concentration increases (compare 1x to 2x).

as a single, well-mixed compartment where blood concentration is equal to the concentration in all other tissues. All kinetic processes are assumed to be first order, meaning that there is no saturation at any stage of the chemical's metabolism. The time-course of the chemical's blood concentration will resemble Figure 2. At the outset of exposure, $\boldsymbol{C}_{\text{blood}}$ will be zero, but begins to rise as inhaled chemical equilibrates with the blood as blood is perfused through the lungs. Initially, the increase in concentration will be nearly linear with time, but gradually begins to plateau as the chemical within the body approaches equilibrium with the external air, and eventually a steady state concentration ($\boldsymbol{C}_{\text{ss}}$) is reached at which new uptake exactly balances removal.

If the air concentration were twice as high (i.e., 2x), the time-course would look similar, but would be shifted upward proportionally to the change in chemical air concentration, Conversely, if the air concentration were lowered from the original level by a factor of two (i.e., 0.5x) the curve would be shifted down and $\boldsymbol{C}_{\text{ss}}$ would be reduced by half. It is important to note that the *time* it takes to achieve steady state does *not* depend on the air concentration. The time to steady state is controlled by the rate of the absorption of chemical across the alveolar membrane, the blood flow to the lung and the ventilation rate, and the blood: air partitioning, none of which will be altered by the air concentration.

If the toxicity of an exposure depends on achieving a critical internal concentration of the chemical, then a given air concentration will be toxic if the breathing of it continues sufficiently long for the internal blood concentration to increase to the critical level. A lower air concentration will take longer to do so (since its uptake curve is lower) and a higher one will take less time. Moreover, because of the progressively decreasing slope (and deviation from linearity) of the uptake curve as steady state is reached, exposures to low air concentrations will take more than proportionally longer to reach a critical internal concentration. That is, particularly long and low exposures will tend to deviate from Haber's rule in the combinations of duration and air concentration that are equally effective in causing toxicity. This is because Haber's rule is only relevant in the initial stages of exposure, where the relationship between internal dose and time is approximately linear. At later stages of exposure, the internal dose approaches steady state conditions and Haber's rule becomes an inappropriate basis for dose-extrapolation.

Note that the exposure duration needed to reach steady state is *not* the same for all compounds. Different chemicals will have different blood:air partitioning, different metabolism, and different volumes of distribution, and so they will take different lengths of time to reach steady state during an inhalation exposure. Thus, the realm of exposure durations that deviate from Haber's Rule will depend on these chemical-specific properties.

This general insight has been developed into a more comprehensive theoretical framework for acute inhalation dosimetry, and Rhomberg (2005) has shown how to derive alternative versions of Haber's rule that incorporate information on the speed with which a compound reaches the internal steady state concentration.

4. Physiologically-Based Modeling

Haber's rule represents a simplistic generalization of chemical behavior. If data are available or can be readily obtained, an alternative is to conduct compound-specific toxicokinetic modeling. Advances in modeling software and increased availability of training in toxicokinetics have made constructing such models accessible to most scientists with basic training in toxicology. Depending on the specifics of the compound, models can be either empirically- or physiologically-based (the former envisioning the body as a number of abstract compartments with transfer between compartments governed by empirically-derived rate constants; the latter incorporating actual physiological data on organ size, blood flows, tissue partitioning, and metabolism). It must be stressed that such models need not be so complex as to predict chemical concentrations in each and every part of the body but only provide accurate predictions in the tissue(s) of interest (e.g., blood, exhaled air). The use of toxicokinetic models facilitates extrapolation of data across species and, perhaps more importantly, across different time intervals (assuming the same metabolic pathways prevail across time frames or at least that the differences are known).

This concept is exemplified in modeling done to predict safe human exposure limits for fire suppression chemicals (Vinegar et al., 2000). Many of these chemicals share the property of cardiac sensitization, i.e., rendering the heart more sensitive to the acute effects of adrenalin and thereby increasing susceptibility to myocardial infarction in stressful situations (Reinhardt et al., 1971; Brock et al., 2003). Emergency personnel could potentially be at risk from exposure to such agents when responding to a fire. It is important to note that the cardiac sensitization effect is entirely acute in nature (the increased sensitivity to adrenalin is lost soon after exposure ceases) and exhibits a clear threshold. The critical determinant of the effect appears to be the attainment of a blood concentration of chemical above the critical value (Vinegar et al., 2000; Brock et al., 2003).

A model was constructed using cardiac sensitization data obtained in dogs, the preferred test species for cardiac sensitization (Vinegar et al., 2000). To develop a model to predict metabolism in humans, both standard human physiological data (blood flows, organ volumes, ventilation rates) as well as novel partitioning data using human blood were obtained. Metabolism of the compounds was measured in rodents and then allometrically scaled to humans. Blood concentrations of the fire retardant chemicals were estimated for 5 min of exposure, the same time frame used during the canine cardiac sensitization test. Brock et al. (2003) note that a model with a similar structure had been used to predict Halon 1211 concentrations in two humans who experienced extreme exposures during a military exercise. The predicted blood concentrations of Halon 1211 were consistent with the outcomes for the two individuals (one of whom died from cardiac effects).

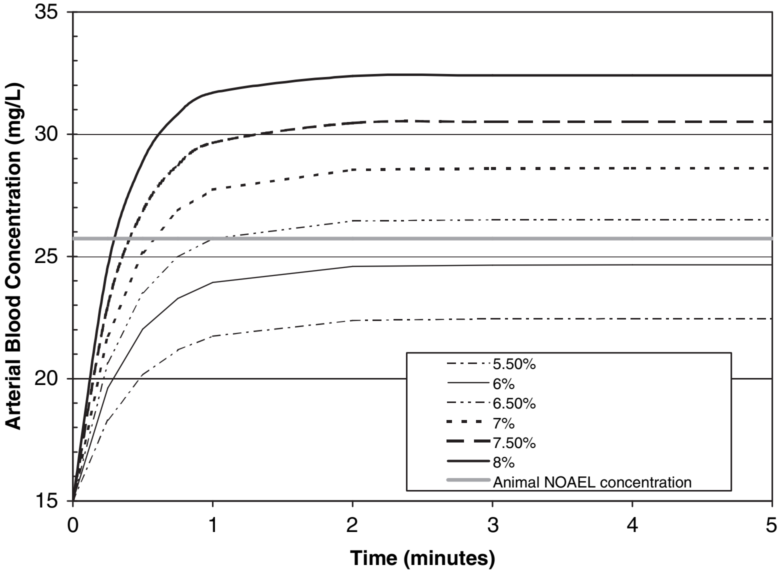

Figure 3. Toxicokinetic modeling prediction of arterial blood concentrations of Halon 1301 for humans exposed at different concentrations (adapated from Vinegar et al., 2000). The solid gray line indicates the no adverse effect level in a cardiac sensitization study in dogs.

TABLE 1. Human exposure time limits established for Halon 1301 based on toxicokinetic modeling.

Concentration (% v/v)	Exposure Time (min)	C × T
6.0	5	30
6.5	1.33	9
7.0	0.59	4
7.5	0.42	3
8.0	0.35	3
Data corresponding to the lowest effect level in the dog cardiac sensitization study		
7.5	5	37.5

Modified from Vingar et al., 2000

The results of the modeling for one particular fire retardant, bromotrifluoromethane (Halon 1301), are shown in Figure 3. At all of the concentrations evaluated, the compound exhibits 1st order uptake and elimination kinetics (similar to the theoretical compound results shown in Figure 2). Steady-state concentrations are quickly attained in about 2 min regardless of the air concentration. These blood concentration-time predictions were used by Vinegar and colleagues to establish exposure limits for time frames ranging from 35 s to 5 min. This required the assumption that the cardiac sensitization data obtained in the dog model is a safe predictor of risk in humans, a position that has been endorsed by the U.S. National Research Council (2004). Interestingly, had the authors attempted to use Haber's rule to extrapolate between different concentrations, the results would have been different, as shown in Table 1. Applying the Haber's rule constant derived from the animal data (i.e., 37.5) across the timeframes of interest would have greatly overestimated the safe exposure time at the higher concentrations. Note also that the value of k based on the time frame permissible at a 6% concentration (i.e., 30) is ten times higher than the value pertinent for the 7.5% and 8% concentrations.

5. Conclusions

As noted earlier, the need to establish acute exposure levels for various types of exposure is a re-emerging priority in risk assessment. In order to achieve this goal, it is necessary to understand the basic toxicological differences between acute and chronic exposures, particularly the role of the mode of action. Understanding a chemical's toxicological MOA can aid in developing biologically-robust estimates of risk or acute exposure limits. In the past, developing such acute exposure levels was largely based either on expert opinion or application of principles such as Haber's rule, a concept shown here to have some notable limitations. If approaches such as Haber's rule are used, it is critical that the metabolic profile of the chemical be understood so the limitations of Haber's rule can be discussed and informed judgments regarding acute dosimetry are made. An alternative is the development of toxicokinetic models. Particularly when physiologically-based, these models have the ability to generate biologically-informed extrapolations of target organ chemical concentration for various exposure points. When the results are linked to a biomarker of acute toxicity, such as a critical blood threshold concentration, these models can provide an improved basis for risk assessment.

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MODELING MULTIMEDIA POLLUTION FOR ENVIRONMENTAL EXPOSURE

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Abstract. The contaminants released into the environment can originate human exposure by the transport through the atmosphere, aquatic systems or through soil sub-compartments. The need for tools to predict environmental behavior of chemicals, contaminants and metals led to the development of mathematical models, which are designed to describe the transport and fate of substances under special environmental conditions. A multicompartment modelling approach may be used to predict contaminants concentration in predefined end-points. Each compartment may represent an environmental media: air, soil, water, flora and biota. Also each one of these compartments may be divided into several sub-compartments. For the exposure assessment from contaminants at large contaminated sites, all transfer pathways leading to the exposure of man and vulnerable ecosystems have to be taken into account. A transfer model through the food chain should also be included, whenever it is possible or relevant. For some contaminants, the uptake into vegetation is the major entry route for the transfer into the food chains: contamination of the trophic chain will be a component of human exposure by transferring the contaminants into animal products that are part of the human's diet. By means of a multicompartment model, the various release mechanisms, transport, transfer and uptake processes are described and the concentration pattern resulting from the consequent exposure is simulated.

Keywords: multimedia models, compartment models, exposure, transport and fate

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L.I. Simeonov and M.A. Hassanien (eds.), *Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology*,

1. Introduction

The legacies of past industrial activities continue to be a cause of concern requiring assessment and remedial action. Over the next several decades, a large investment will have to be committed to clean up sites contaminated with hazardous waste and petroleum products all over the world. This commitment will result in a continuing demand for site remediation services and technologies, which implies more research needs.

The special risks associated with chemicals, contaminants or metals in the past were mostly addressed to those under their direct influence. Over the past decades, these concerns for worker's health and safety have been the driving force for gradually tighter controls and improved work and safety practices. Only in relatively recent times, however, impacts on public health and on the wider natural environment have been received the deserved attention. In the case of the natural environment, these concerns include the risk of environmental degradation, contamination and ecosystem biodiversity, aesthetics, access to land and future land beneficial use.

It has been increasingly recognized that the environment should be considered as a system and the influence of contaminants on environmental systems can only be explained by the interaction of many single processes. Understanding and predicting the fate of chemicals and contaminants in the environment requires a scheme of this complex system: a model.

When contaminants are released into the environment they may reach environmentally damaging concentrations and once released they are not longer controllable and may persist for a very long period before any damage is perceptible. The need for tools to predict environmental behavior of chemicals, contaminants and metals led to the development of mathematical models, which are designed to describe the transport and fate of substances under special environmental conditions.

When modeling contaminant release and transport mechanisms for each environmental compartment, the major output chosen is often the contaminant concentration at each exposition point selected. The concentration at the target is called exposure, a term derived from toxicology; the environmental hazard is the product of exposure and its effect. The purpose of modeling is to quantify the potential exposure levels of the hazard at the receptor location by determining concentrations now and in the future in abiotic and biotic environmental segments and recognize endangered ecosystems, populations or organisms (Trapp and Matthies, 1997).

2. Environmental Exposure Assessment

An exposure assessment is the process of measuring or modeling the magnitude, frequency and duration of contact between a potentially harmful agent and a receptor or a target population, including its size and its characteristics. Ideally, it describes the sources, pathways, routes, and the uncertainties in the assessment (McKone and MacLeod, 2003; IPCS, 2004).

The contaminants released into the environment will contribute to human exposure by the transport through the atmosphere, aquatic systems or through soil sub-compartments. Exposures result from the contacts with contaminated air, soils and food which may be dominated by contacts with a single medium or may be the reflection of the contacts with multiple exposure media (McKone and MacLeod, 2003).

Exposure assessment is used in epidemiological studies to relate exposure concentrations to adverse health results. It is also a component of risk assessment, the process that provides scientific information for risk management. Exposure assessment is based on exposure scenarios, which are defined as: "A combination of facts, assumptions and inferences that define a discrete situation where potential exposures may occur" (IPCS, 2004). These may include the source, the exposed receptor, the period of time that the exposure occurs and activities. Each pathway has an associated exposure surface and subsequent rout of intake or uptake.

For exposure assessment all transfer pathways leading to the exposure of man and vulnerable ecosystems should be taken in account. For instance, pasture may be contaminated through direct deposition, root uptake or irrigation with contaminated water. The material resuspension from superficial soil may occur due to the wind, rain or mechanical factors, with later deposition onto vegetation surface.

The important routes of contamination should be identified: the magnitude and relative contribution of each exposure pathway must be considered in order to assess total exposure and to determine the best approach for developing the appropriate models. The true potential for exposure can not be quantified unless the pathways that account for the routs of intake and uptake for the receptor are identified (McKone and MacLeod, 2003). Also, the important chemicals, contaminants and heavy metals should be identified in each environmental compartment based on their chemical, physical and radiological properties. Scenarios are then often created to aid exposure assessors in estimating exposure (IPCS, 2004).

2.1. EXPOSURE MODELS APPLICATIONS

An exposure model is “a conceptual or mathematical representation of the exposure process” (IPCS, 2004). It describes the processes determining the environmental fate of a chemical or contaminant giving, at the same time, the information of its environmental behavior.

The output of an exposure model can be an exposure concentration; in practice, however, exposure often includes estimates of intake as the amount of chemical inhaled or ingested and the amount of a chemical that is absorbed into the body.

Exposure modeling is often complex, and this is well reflected in the diversity of published exposure models that is possible to find in literature. Also, exposure models have recently been developed for a number of different situations (Trapp and Matthies, 1997): control of emissions into air; estimation of the consequences of accidents and catastrophes; as a part of risk assessment of new and existing chemicals; to hazard assessment of contaminated sites; optimization of experiments and monitoring programmes; to determine parameters that cannot be measured directly using inverse modeling.

As we can see, models are developed for many purposes, ranging from the purely academic to providing support for environmental regulations and administrative permit processing. However, there are three main important applications of exposure models: (i) epidemiological studies; (ii) risk assessments to support risk management decisions and (iii) assessment of the efficacy of environmental risk management policies.

The power of exposure models is often overestimated. Models can certainly help to give a range of results under plausible assumptions and thus may support decisions, but we must be aware of the fact that the environment is a complex and open system with extreme spatial and dynamic variability and consequently are limited (Trapp and Matthies, 1997). Simplifications, neglecting and idealizations are necessary, depending on the question, the problem, the data availability and the quality which implies uncertainty, sparse data, missing data, non-representative data, expert judgments, etc. (Trapp and Matthies, 1997).

2.2. ENVIRONMENTAL EXPOSURE PURPOSES

Many exposure assessments are based on exposure models that combine measures and assumptions to generate an estimative of concentrations or rate of intake. Exposure models can be developed to estimate exposures and doses of individuals, defined population groups or entire populations which may be estimated as a continuous variable or integrated over time ranging from minutes to a lifetime. The modeled outputs may include mean or median values, distribution parameters (standard deviations, quartiles, ranges) or complete probability density distributions. Consequently, exposure models vary widely in complexity, approach, inputs and outputs (IPCS, 2005).

For environmental exposure assessment, several steps should be followed to achieve the defined purpose and a set of questions or requirements should be answered or fulfilled (Trapp and Matthies, 1997):

- What are the purpose and scope? Is there an accidental release (short emission with high concentration) or a continuous long-term contamination? The level of detail needs to be established; which period of time is simulated? Which contaminant, chemical or chemical class is considered?
- Identification of underlying physical, chemical and biological processes: contaminant release, transport, chemical reactions, adsorption, transformation, biodegradation and bioaccumulation.
- Formulation of mathematical equations and model development: the processes need to be translated into mathematical terms, the model is usually consisted of a set of differential equations, where concentrations are the differential vectors and processes describing their changes; a simulation language may assist programming.
- Data acquisition: exposure models require either contaminant data or environmental data. Many times these data are no directly available but estimated from other data by empirical relations.
- Verification and calibration of the model structure which means testing the underlying process description. This is done by using experimental data from selected reference contaminants or site and calibration is fitting certain model parameters using these measurements.
- Sensitivity analysis of parameters depends strongly on environmental and chemical data and must be determined for the specific problem. One way of doing this is the variation of the input parameters analyzing the correlation with the output: sensitive parameters show a high correlation.
- Validation is the result of the comparison between independently measured concentrations and the results of model simulation. It should be noted that the validation strongly depends on its purpose.
- Uncertainty analysis (lack of accuracy): the uncertainty of model also comes from the variance of input data (stochastic error) as well as from inadequate model structures (for instance, systematic errors due to oversimplification). Stochastic errors can be estimated or calculated by stochastic methods (Monte-Carlo) while systematic errors are more difficult to quantify.

- Decision and documentation: a report should always be prepared stating the question to be answered and the work that has been done. Without documentation and publication, all work must be repeated when a similar problems occurs.

3. Exposure Models Approach

An exposure model is a structure designed to reflect real scenarios and processes. A frequently and successfully applied approach in exposure modelling is the division of the environment into compartments connected between them. These compartments are assumed to be homogeneously mixed with a defined geometry, and therefore defined volumes, masses and densities, and to exchange chemical substances and energy between them.

Several assumptions are done so that systems in physical existence can be modeled mathematically. After mathematically modeled, the system can be coded into simulation programmes developed in one of many existing computer languages.

A conceptual model is often illustrated by a set of these compartments defining the physical and chemical information and exposure algorithms by which the model reflects a realist exposure scenario: the implementation of an exposure model should reflect the underlying conceptual model.

Every compartment has a number of connections going into (inflows) and a number of arrows leaving the compartment (outflows). Material can either flow from one compartment to another, it can be added from outside through a source, or it can be removed through a drain or a sink.

Most compartment models have more than one compartment and the necessary equations to describe the transfers between the compartments result from the application of a conservation law for each compartment: conservation laws state that the difference between what flows in and what flows out quantify how much material will be stored in the compartment. The resulting relationship between inputs and outputs is described by algorithms, equations and intermediate variables. The system should be faced as a whole, where the parameters representing the material in the compartment (the state-variable) will depend on what flows in and what flows out (Blomhøj et al., 2005).

The important thing to retain is that the development of the conceptual model will determine how the model parameters and variables, in a consistent way, will depend on each other (Blomhøj et al., 2005).

4. Multimedia Models

Air, water, sediments, soil, flora and biota may be considered generic environmental compartments. Each one of these compartments may also be divided into sub-compartments. Contaminants in general may travel through the atmosphere, soil, surface water and groundwater affecting the organisms that inhabit these media.

The multimedia concept focuses its attention on the long-term behavior and effects of chemicals released from modern industrial facilities into the environment. Organic-chemical, inorganic-chemical and radionuclide contamination of soils, the release of volatile and semi-volatile organic compounds to air and to soil, and toxic-chemical runoff to surface water are all multimedia problems (McKone and MacLeod, 2003).

The multimedia approach applied to exposure modeling quantifies the impacts of contaminants, as they travel through more than one of the environmental compartments, quantifying contaminants concentration in predefined end-points or exposure receptors. Exposure models combine modeled exposure concentrations and information about the target or receptor to estimate some measure of exposure or dose (IPCS, 2005).

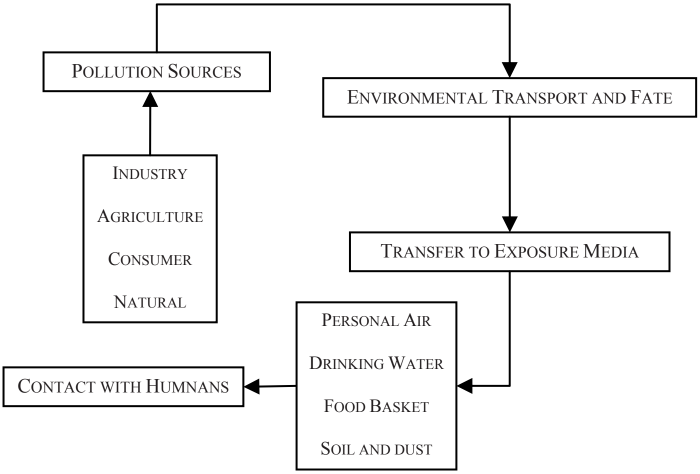

Figure 1. A conceptual illustration of the migration of pollutants from sources, through the multimedia environment and into exposure media, followed by contact with humans. (From McKone and MacLeod, 2003.)

An environmental fate model is implicit in a multimedia model as describes the dynamics of the transport and transformation of a chemical or contaminant in a specific environment taking into account the physical, chemical and biological processes which affect the quantity, structure, concentration and properties of the chemical on the considered spatial temporal scale.

Fate and transport models are used to predict the movement of contaminants between and within compartments. A fate model is a mathematical converter which transforms input rates (Mass/Time) into concentrations (Mass/Volume) under specific assumptions, initial and boundary conditions (Trapp and Matthies, 1997). It is composed of equations and parameters; the equations describe quantitatively the natural processes being modeled, usually as equilibrium or rate expressions, and the parameters describe relevant properties of the specific system under investigation. These parameters can be classified as chemical properties, discharge or emission data, and landscape parameters. Together the equations and parameters produce the model results (Webster and Mackay, 2003).

Considering to fate model scale, two different approaches may be used: small scale and large scale models. Small scale models, also known as local fate models, are those concerned with the environment close to the release site, the dominant processes are physical, like advection, dispersion, mixing and dilution and a local model is usually a single medium model. In a large scale approach, global fate models are those which are concerned with large scale behavior, the important processes are chemical equilibrium and transformation reactions, like partitioning, degradation and diffusive mass transfer and a multimedia model is the most appropriate representation. In an intermediate level, there are regional scale models or regional fate models which focus on the scale in between these two extremes, thus all environmental processes and factors have to be considered. This is the most complex problem as the description of contaminants in a regional scale reveals many difficult quantitative problems: many different variables, which are often not available, may be required.

5. Intercompartmental Model

An intercompartmental model relies on developing mathematical models based on a direct or indirect exposure model to a contamination source. The mathematical models should describe the: (i) dynamic equilibrium; (ii) release mechanisms; (iii) transport mechanisms and (iv) transfer phase processes.

First, a systematic analysis should be performed in order to consider the integrated approach of the following points: sources; release mechanisms; transport mechanisms (by dispersive vectors like air and water); transfer mechanisms between the environmental compartments; estimative of concentrations in each environmental compartment using dispersion models with spatial variation;

definition of the privileged exposure points and identification of exposed receptors (IPCS, 2005; Robinson, 2006). A conceptual model will be generated at this stage defining physical, chemical and behavioral information and exposure algorithms, describing the objectives, inputs, outputs, content, assumptions and simplifications adopted, by which the models translate a realistic exposure scenario. The next step is to convert the conceptual model into several mathematical models, build the simulations programmes and code them into one of many existing computer languages. To calibrate the models and for its validation it will be necessary to use direct extensive measurements from a contaminated site. For the modelling exposure it will be necessary to perform several model simulations and evaluate the interaction between reality and models results.

A vast number of sub-models can be generated in a multicompartmental model leading to a multipathway exposure relating contaminant concentrations in multiple environmental media to concentrations in the media with which the receptor has contact (for example, breathing air, tap water, foods, household dusts and soils). The potential for harm is assessed either as the average daily intake or uptake rate or as time-averaged contact concentration (McKone and MacLeod, 2003). Exposure models for each environmental compartment quantify the resulting concentration in exposure points resulting from: release and transport in air; release and transport in underground water; transport and transfer in surface water; transfer to vegetation and transfer through food-chain. These processes will be review in detail in the following sections.

5.1. AIR CONTAMINATIONS SOURCES

Chemical substances are released into the atmosphere from several sources: traffic, industry, households, heating systems, power stations and pesticides applications. Contaminants may be discharged to the atmosphere by particle suspension, venting from containers and volatilization from water and soil. Often contaminated sites have gaseous releases to the outdoor or ambient air leading to the resident's exposure from the vicinity of the site. In this case, the contaminant concentration is estimated at the air breathing height defined to be at 1.7 m above the ground which corresponds to the inhalation height. Once released, contaminants will disperse downwind and deposit on ground surfaces in a pattern dependent on the local meteorology, the nature of the terrain downwind of the release and the physical and chemical characteristics of the emission. Exposure to humans can occur by inhalation or by ingestion resulting from consumption of contaminated water, crops, and animals (EPA, 1996).

In the atmosphere, chemicals are transported by diffusion/dispersion and advection and are eliminated by deposition or photo degradation. Atmospheric dispersion models are the mathematical simulation of how air pollutants disperse in the ambient atmosphere. The dispersion models are used to estimate or to predict the downwind concentration of air pollutants emitted from sources.

In atmospheric modeling two different approaches may be adopted for emission source: calculation of atmospheric transport and fate following area and point-source emission. For the area source it is normally used a steady-state model with dilution by the wind and elimination both by deposition and degradation. Typical examples are the diffuse urban emissions or spraying of pesticides. In one single compartment box model, the release area is rectangular and is assumed to be the sum of many sources (Figure 1). For point emissions a local plume model is used, with dilution by atmospheric dispersion. Concentrations downwards from point sources are calculated using a Gaussian model. It is a solution of the three-dimensional dispersion advection equation. Advection is due to the wind; dispersion is caused by atmospheric turbulence (Figure 2).

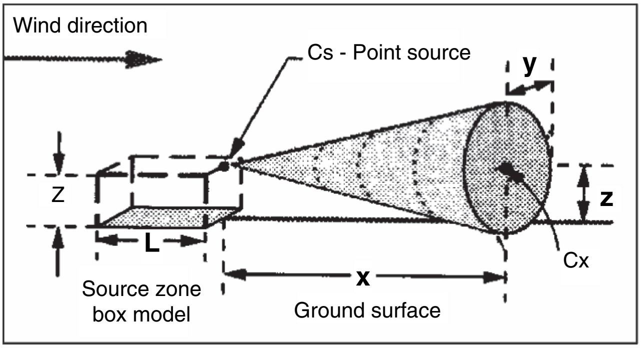

Figure 2. Release area and contaminant dispersion.

5.2. TRANSPORT IN GROUNDWATER

Often ground water is an important pathway for contaminations found below the soil surface. Contaminants leach from the waste, move downward through the unsaturated zone to the water table and then migrate in the saturated ground water system. The contaminants may discharge either to a drinking water well or to a surface stream. Humans are exposed to contaminants by using well water or surface water and by eating organisms living in the surface streams.

Most groundwater models quantify the vertical movement of contaminants and provide inputs to contaminant transport models in aquifers. Simulation may provide contaminant behavior in groundwater and quantitative assessments for environmental decision making.

At specific sites, groundwater models are used to estimate the travel times and concentrations of contaminant plume from source to drinking-water well or surface water. They are used to identify vulnerable aquifers and to select locations for monitoring wells used to collect data for exposure assessments (IPCS, 2005).

In a typical saturated zone model, the aquifer is assumed to be a relatively homogeneous matrix of solids and pore spaces through which contaminants move in dilute solution with the flow of the water. A mass balance equation describes the water flow in terms of the permeability of the aquifer material (given by the hydraulic conductivity) and the force of gravity (given by the hydraulic gradient). Attenuation processes such as sorption to aquifer material, biodegradation and chemical reactions may be included as well as retardation (IPCS, 2005).

Outputs can be presented as concentrations describing the groundwater plume at various times after the contaminant enters in the system. Geographic Information System (GIS) technology can be used to represent the groundwater plume at various stages as it spreads and enters in drinking-water aquifers, well water and surface water supplies (IPCS, 2005).

On the other hand, the pores of the unsaturated zone are filled with a mixture of water and air. The model for solute transport in the unsaturated zone is similar to that for saturated flow. Attenuation and retardation processes as well as losses of water and contaminant at the surface through runoff, soil erosion, uptake by plants and evapotranspiration may be included. Major output of the unsaturated zone model is the pore water solute concentration and can be used as input to a groundwater model with the solute containing the leachate being the recharge to the aquifer in the saturated zone model (IPCS, 2005).

5.3. SURFACE WATER MODEL TRANSPORT

Surface water may be an important pathway by which contaminants are transported from a contaminated site; such pathways include lakes, streams, rivers, and the rainfall-runoff process. Contaminants present on the surface of a contaminated site may be carried as suspended particles or dissolved in surface runoff and be transported to adjacent bodies of surface water.

By modeling contaminant transport and fate and estimate concentration in lakes, streams, estuaries, and marine environments, researchers can better understand how exposure to contaminants affects aquatic environments. Exposure to humans can occur through drinking and using contaminated surface water or by eating organisms living in these water bodies (EPA, 1996).

Surface water models are based on the concept of conservation of mass expressed by mass balance equations. A system is defined like a stream or lake segment and specifies its boundary conditions and the way the contaminant enters into the system. Contaminants may enter in the system by point source release or non-point sources (urban or agricultural runoff and soil erosion, dry deposition contained sorbed chemicals, etc.) (IPCS, 2005).

The simpler approach of the mass balance model for a stream assumes that a contaminant enters in the stream at a specified point with a constant rate and at some point it is instantly well mixed. Concentration is calculated by dividing the release rate in mass per day by the stream's volumetric flow rate.

More complex models allow describe release rate variation with time and include processes such as: partition (total concentration results from dissolved chemicals and chemicals sorbed to particles), degradation (hydrolysis, photolysis and biotic transformations; all first order reactions), volatilization (expressed as the elimination rate for total concentration), sedimentation (exchange of a chemical between a water body and sediments have an extreme spatial and dynamic variability). These processes will make part of the model equations in which all elimination pathways are expressed as first order rate constants. Other important processes that may be considered in the model are dilution, advective transport, sorption to suspended particles and deposition of particles.

5.4. SOURCES TO SOIL CONTAMINATION

The major sources to soil contamination derive from four main groups: (i) atmospheric emissions from the traffic or industry either by deposition onto soil surface as particles or as gaseous compounds having as for consequence the contamination of large areas with various types of pollutants (heavy metals, persistent organic chemicals, acids); (ii) agriculture chemicals (pesticides and mineral fertilizers are applied in most agricultural systems); (iii) waste water discharged directly to fresh water or salt water, irrigation with contaminated water (if polluted water from contaminated wells, for example, is used as irrigation water or if natural or artificial flooding occurs, chemical pollutants can enter the soil), application of sewage sludge to soil as fertilizer is responsible for considerable amount of heavy metals in soil; (iv) solid wastes (industrial and households) have been dumped into shallow soils or deposited onto the ground (Trapp and Matthies, 1997).

Soil contamination can pose risks to soil organisms as well as other ecosystems; plants (grow in contaminated soil take up the contamination through their roots); animals and humans (by ingestion, inhalation or contact with contaminated soil, plants or animals).

The transport and fate of substances in soil are mainly controlled by: advection (with soil and water) and leaching into groundwater; dispersion/ diffusion in gas and water filled pores; sorption to the soil matrix; biotic and abiotic degradation or transformation; uptake by plants and volatilization into the atmosphere. Mixing of chemicals may also occur by soil organisms (Trapp and Matthies, 1997).

5.5. PLANT UPTAKE

There are several ways to terrestrial plants be contaminated. Uptake may be from polluted soils by former waste dumps or industrial sites or from air due to deposition (leaves, in particular, will be exposed to airborne contaminants).

Vegetation may be contaminated through direct deposition, root uptake or irrigation with contaminated water. The material resuspension from superficial soil may occur due to the wind, rain or mechanical factors, with later deposition onto vegetation surface. Each one of these contamination pathways should be considered in the model. Modelling contaminants transfer to vegetation has implicit several processes which describe and quantify mathematically the uptake into roots, translocation into shots, gaseous deposition on leaves, volatilization from leaves, metabolism and degradation processes and dilution by exponential growth. The different contamination processes should then be combined in a global model for simulate the contaminant transfer from each one of the contamination processes. The final output is the total concentration in the vegetation expressing internal and internal contamination. The main goal is to develop a contaminant transfer model through food chain by the ingestion of contaminated vegetation by an organism of a relevant trophic level.

5.6. FOOD-CHAIN MODELS

Food chains are biosphere pathways through which humans are exposed to environmental contaminants. They represent the contaminants bioaccumulation in animals and plants that are affected by their release and dispersion from the contaminated site. For instance, deposition can be a significant pathway to human exposure by first ingestion of contaminated pasture by animals and then by the ingestion of animal products contaminated (dairy or meat). As a consequence of food-chain models, contaminated aquatic and terrestrial environments typically result in the bioaccumulation of chemicals within all trophic levels of an ecosystem. Software models provide tools for tracking the movement of contaminants through food chains and for estimating impacts on exposed biota.

One of the typical terrestrial food chain usually considered for modeling exposure results from the relevant incorporation of contaminants in the transfer pathway *pasture-cow-milk*. A dynamic multicompartmental model may be used to describe contaminants behavior in this exposure route and predict the concentration in each compartment following an initial contaminant deposition. The number of compartments to consider will depend on the conceptual model adopted and the detail considered. This will determine the number of differential equations of the system as for each compartment a transient mass balance equation defines the relations between the inner transformations and the input and output fluxes.

In the mathematical models, the equations system can be represented in a matrix form with constant coefficients and solved numerically with appropriate software to obtain the concentration in each compartment. The final output is the concentration variation with time for each compartment. The concentration values within each compartment may be then transcribed to doses values based on a simplified exposure pathway and a predefined critical group.

6. Case Example

The situation to be modeled is the release of a gaseous or particulate substance from a contaminated site. The case of radon dispersion in air was considered for this example. Radon is a colorless, naturally occurring radioactive noble gas that is formed from the decay of radium and it is easily dispersed by wind. It is found in many natural materials, such as soil, rocks, well water, and building materials and is considered to be a health hazard as the exposure may cause lung cancer. Most of the analytical solutions for radon transport mechanism are based on the Pasquill-Gifford model (Dinis and Fiúza, 2005). It is assumed that the release is a constant point source that creates a “plume” dispersion. The downwind concentrations are estimated based on the following assumptions:

- The contaminated site was defined as a conceptual regular polygon area representative of one or several uniform area sources with the same mass flux as the entire affected zones; the release point is located in the weighted centre of the polygon area.
- The contaminant concentration released from the contaminated site is estimated by a box model formulation: a steady state assumption is adopted and therefore the pollutant concentration is constant in time; the mass flow rate entering into the box is equal to the flow rate leaving the box.
- The atmospheric dispersion is modeled by a modified Gaussian plume equation, represented by the equation of Pasquill as modified by Gifford (Dinis and Fiúza, 2005), simulating the average dispersion of the contaminants released from the source in each wind direction to a downwind receptor. The dispersion along the direction of wind flow will generate a plume due to the continuous material release.

- The concentrations along each wind direction are evaluated taking into account the respective mean wind velocity and the frequency of the occurrence. This will lead to different concentrations in the sectors defined by each direction in the collateral wind rose.
- The concentrations are distributed as a Normal Distribution (Gauss) in the horizontal and vertical directions relative to the wind direction. The atmospheric dispersion coefficients, σ_y (m) and σ_z (m) are actually the standard deviations of the plume concentration in the horizontal and vertical directions, respectively.
- For calculations exclusively in the dominant wind direction, it is assumed that all the contaminant concentration is being distributed in that direction, being inexistent in all other directions. Another assumption is that contaminant concentration is uniform in the volume defined by the central point source and the boundaries of the release area, and by the mixing height. Dispersion occurs outside this area.
- Constant wind speed in each direction is assumed in the simulation. For large release events this may not be reasonable. It is however, a reasonable first assumption in most situations that simplifies the calculations.

The applicable equation describing concentrations dispersion at ground level, given a plume release at height H, is (Dinis and Fiúza, 2005):

$$X = \frac{Q}{2\pi\mu\sigma_y\sigma_z} e^{\left[-1/2\left(\frac{y}{\sigma_y}\right)^2\right]} \left\{ e^{\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]} + e^{\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]} \right\} \tag{1}$$

This equation represents a Gaussian distribution, where X represents contaminant concentration, Q is the source strength, H (m) is the corrected source released height and σ_y (m) and σ_z (m) are the dispersion parameters in the horizontal and vertical directions, respectively. The dispersion coefficients are determined based on the atmospheric stability class and the distance from the source. The values are available in many air pollution texts as log-log plots of dispersion coefficient vs. distance. There are six stability classes; each one has a different curve on the dispersion coefficient plots. The atmospheric stability classes range from class A, which is the most unstable, to class F which is the most stable. The classes depend upon the average wind speed at a height of 10 m, the amount of incoming solar radiation during the day and the amount of cloud cover at night.

Data is needed for average wind speeds, frequency and directions for the particular study location. These data were obtained from a local automatic meteorological station, “Mesquitela”, integrated in the National Information System of Water Resources Database (INAG, 2003).

The regular polygon area was divided into eight sectors as that national meteorological data set refers to octants. Each sector has a characteristic average wind speed and frequency in the following directions: N S E W NW NE SE SW. The registered values fit in the Pasquill stability class D (neutral) so this was chosen to estimate the typical dispersion coefficients. Other parameters necessary for the simulation were adopted from a few local measurements made in the contaminated site, known as “Cunha Baixa”, located in the Central Portugal (Vicente, 2005). The contaminated site has a total area of approximately 91,993 m^2 being composed by four distinct areas with different radon release: the radon flux was calculated for the global area, now conceptually defined as a regular octagon. This area contains more than 1.1 Mt of wastes radiological different and also with different composition.

We defined a 2-km distance from the centre for simulating the concentration dispersion in each wind direction; the same distance was considered for the dominant wind direction. The model was implemented in Matlab and the concentrations were calculated in each sector according to the wind directions considered. The output includes the maximum centerline concentration at the given distance and at the x and y coordinates of the receptor point exposed. This provides the information needed to determine if the pathway will be important, compared with other pathways, in a detailed analysis. The dispersion results in each wind direction can be seen in the figures below (Figures 3 and 4) .

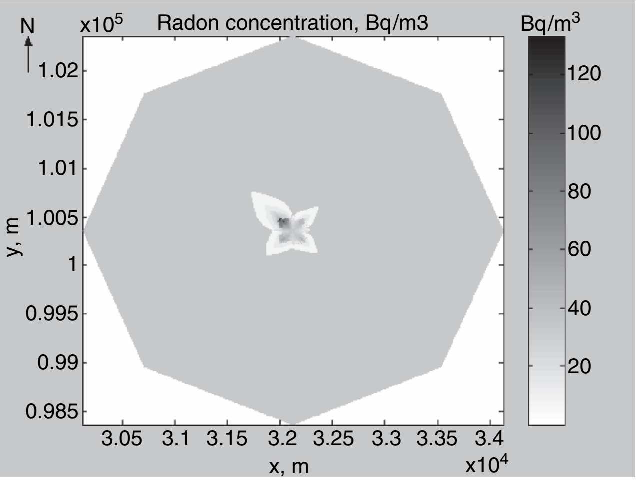

Figure 3. Radon dispersion in each wind direction, Bq m^{-3} (Cunha, Baixa).

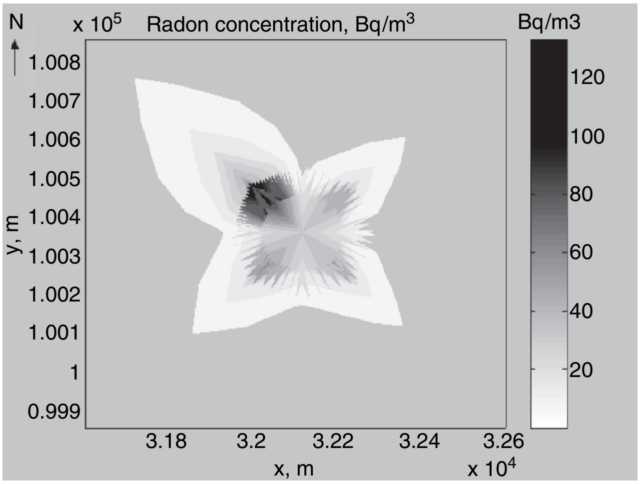

Figure 4. Radon dispersion in each wind direction amplified, Bq m^{-3} (Cunha, Baixa).

From the previous figures we can see that the dominant wind direction is to Northwest (NW). The concentration at the breathing height in this direction refers only to the boundary side that limits the respective sector. The dispersion results can be seen in the figure below (Figure 5).

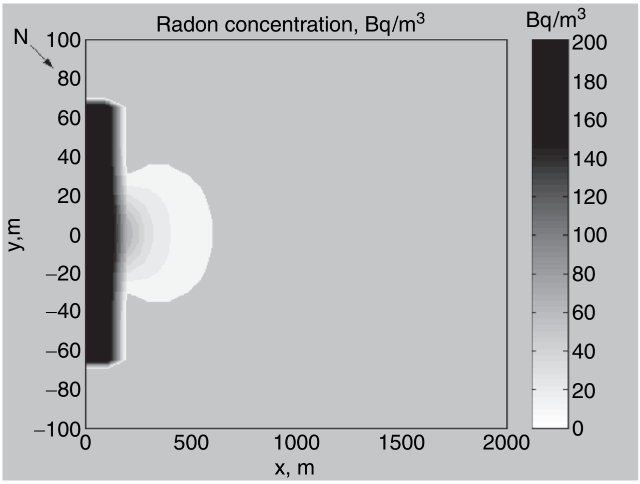

Figure 5. Radon dispersion in the dominant wind direction (NW), Bq m^{-3} (Cunha, Baixa).

This model was applied to other sites with the same contamination but with different meteorological and local conditions and also radon release flux. The two sites considered are known as Urgeiriça and Castelejo sites and are also located in central Portugal; this region had an intensive uranium mining during almost a century resulting in 13 Mt of different wastes dispersed in open-air areas.

For the Urgeiriça site an old dam with 2.5 Mt occupying an area of 13.3 ha containing uranium tailings from the sludge mill facility, is the major contamination source due to high radium content responsible for the radon release. The contaminated site is composed by seven different areas with radium content ranged from 3,400 to 66,000 Bq kg^{-1}.

Local wind speed and frequency were adopted from "Nelas" meteorological station. The registered values also fit in the Pasquill stability class D (neutral) which was adopted to estimate the typical dispersion coefficients. The figures below (Figures 6, 7 and 8) show the results of model simulation in each wind direction and in the dominant wind direction also. The dominant wind direction is to Northeast (NE).

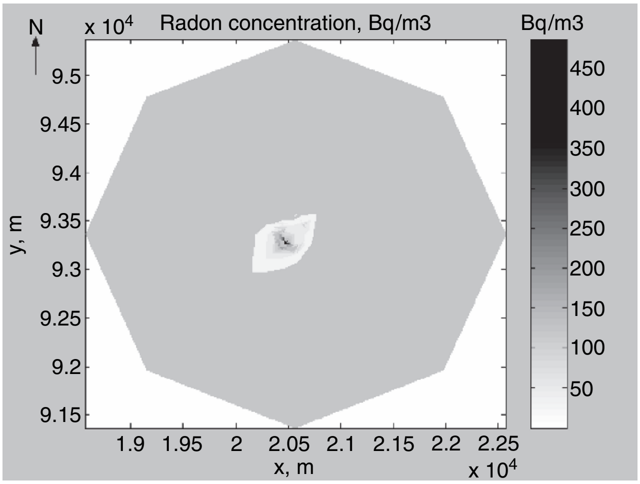

Figure 6. Radon dispersion in each wind direction, Bq m^{-3} (Urgeiriça).

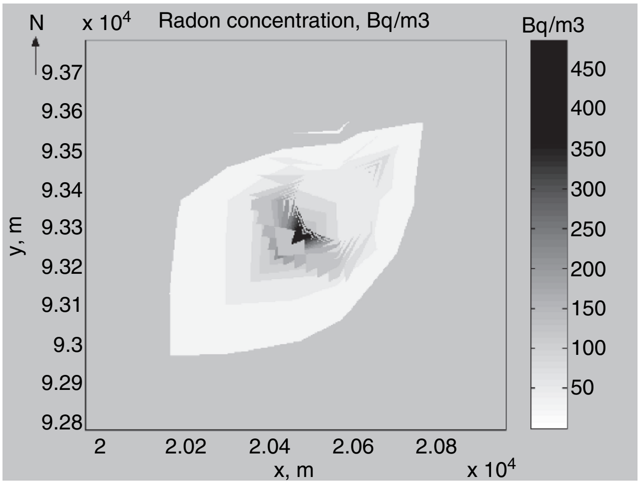

Figure 7. Radon dispersion in each wind direction amplified, Bq m^{-3} (Urgeiriça).

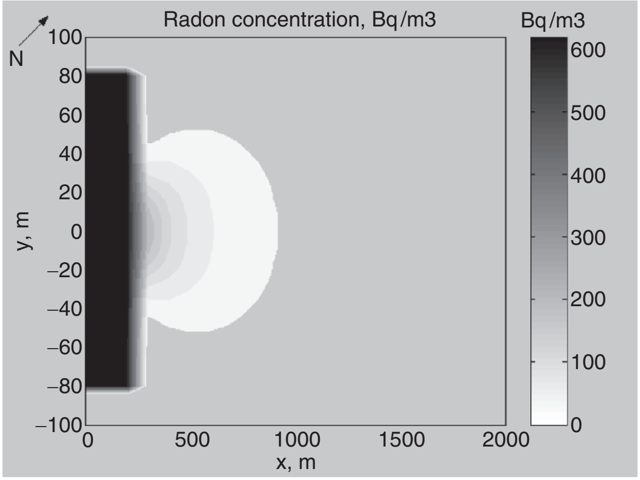

Figure 8. Radon dispersion in the dominant wind direction (NE), Bq m^{-3} (Urgeiriça).

For the Castelejo site two dams with low grade ore, waste rock material and natural geological material represent the contamination source. Some of these materials were used in the past for road construction and maintenance (Vicente, 2005). The area considered for modeling the radon release and dispersion from Castelejo site was 73,835 m^2. Local wind speed and frequency were adopted from "Penhas Douradas" meteorological station. The registered values also fit in the Pasquill stability class D (neutral). The figures below (Figures 9, 10 and 11) show the results of model simulation in each wind direction and in the dominant wind direction also. The dominant wind direction is to Southeast (SE).

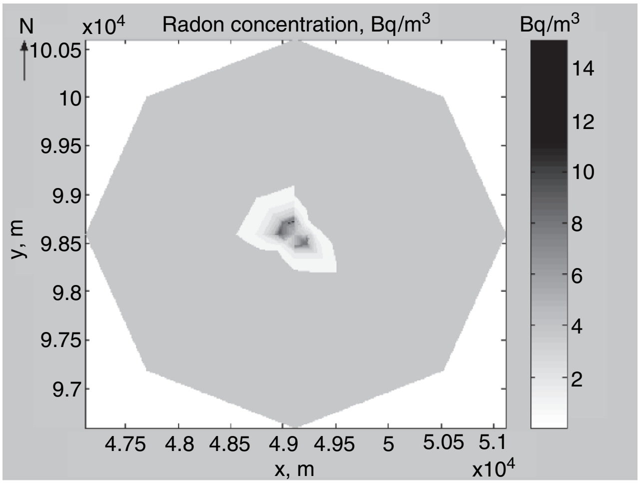

Figure 9. Radon dispersion in each wind direction, Bq m^{-3} (Castelejo).

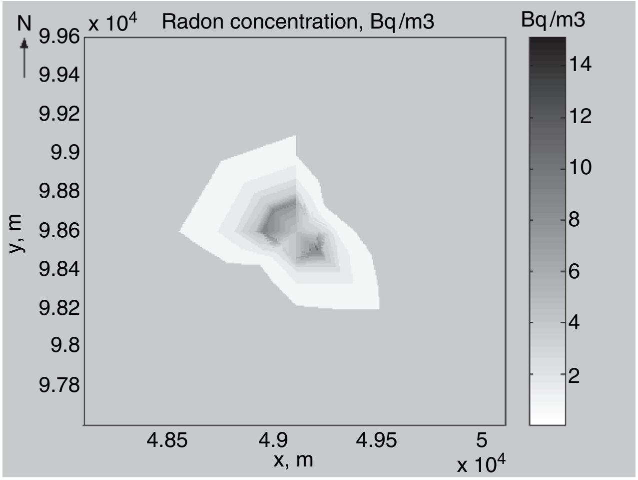

Figure 10. Radon dispersion in each wind direction amplified, Bq m^{-3} (Castelejo).

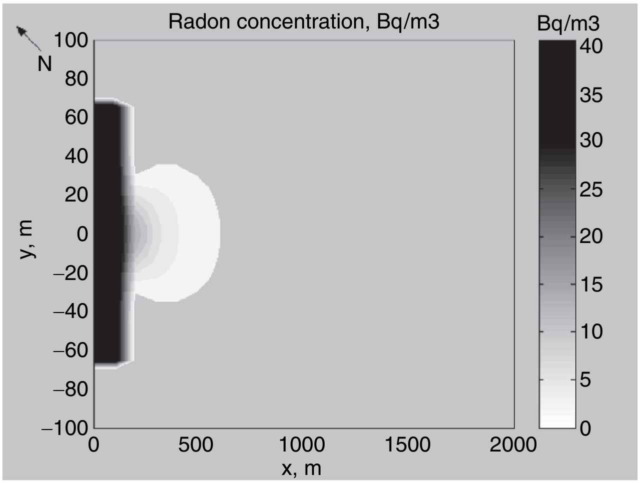

Figure 11. Radon dispersion in the dominant wind direction (SE), Bq m^{-3} (Castelejo).

7. Discussion and Conclusions

A model is a simplified mathematical representation of a real situation to be modeled based on reasonable assumptions and aggregated descriptions, model structure uncertainties and assessor uncertainty. A model should be flexible enough to adequate represent relevant environmental processes, according to up-to-date knowledge of the environment; however, excessive model complexity may result in limited reliability as a higher number of uncertain and/or variable input parameters usually decrease the accuracy of model predictions.

While multimedia models are an indispensable tool in many situations, these models are highly complex and multiple scientific judgments go into their construction and use which can have significant impacts on model performance. As a consequence, multimedia exposure assessments that estimate total exposures via all pathways and routes are more complex and costly than single medium assessments (IPCS, 2005). A multimedia model implies a multicompartmental approach and as the number of compartments increase, the model can be very complex and the solutions usually beyond ordinary calculation. Generally speaking, as the number of compartments increase, it is challenging both to find the algebraic and numerical solutions of the model. However, there are special cases of models that rarely exist in nature, when the topologies exhibit certain regularities that the solutions become easier to find.

The quality of a model is not measured by its complexity, but by the gain in knowledge. This implies that the number of the system components, the compartments, should be as small as possible. The model should only include the considerably important processes. It should also require a minimum of data and be comparable with experimental results. Taking as a general rule: modeling should be kept as simple as possible; the shorter the exposure pathway to be modeled, the lower is the uncertainty introduce by the modeling process (Kirchner and Steiner, 1997).

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RISK ASSESSMENT OF MIXTURES OF CHEMICAL POLLUTANTS IN THE ENVIRONMENT

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Abstract. Environmental contamination problems are complex issues with worldwide implications. Risks to human and ecological health as a result of toxic compounds and their introduction into the environment is a matter of great interest to modern society. Ecological risk assessment and the human health risk assessment are the two related activities of which the environmental risk assessment is comprised. Mixtures of pollutants can contain all type of chemicals: organic, inorganic, organometallic in gaseous, liquid or solid state. This paper presents the steps to be carried out in order to perform the risk assessment for environment and human health. Exposure assessment is detailed by the presentation of original results obtained in studies concerning the determination of bioconcentration factors (BCF) of six metals (cadmium, chromium, copper, lead, nickel and silver) in the Romanian Black Sea coast, sediments and marine biota, during 2003–2006. The reported BCF allow concluding that at the moment there is no pollution concern in the studied area.

Keywords: risk assessment, bioconcentration factors, traces metals, marine biota

1. Introduction

Risk assessment is a tool used to organize, to structure and to compile scientific information in order to help identify existing hazardous situations, anticipate potential problems, establish priorities and provide a basis for regulatory controls and/or corrective actions (Word Health Organization, 2004). Whereas

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large amounts of toxic substances may be of major concern, simply detecting a hazardous chemical in the environment should not necessarily be a cause of alarm. The intrinsic knowledge of the physical/chemical properties of pollutants, biodegradability, potential of bioaccumulation or potential effects of the chemical substances is necessary for the evaluation of environmental risk (Meneses, 2004; Sutter, 2007).

Moreover, it is necessary to carry out a detailed evaluation of the emission sources, as well as the fate, transport and distribution in the different media. As a consequence, the analysis of environmental samples in the laboratory and the application of mathematical models are vital. Ecological risk assessment and the human health risk assessment are the two related disciplines of which the environmental risk assessment is comprised (Trebse, 2004).

Both ecological and human health risk assessment, involves four steps:

- **Hazard identification** – determination if a chemical, physical, or biological entity that could induce adverse effects on individuals, populations, communities, or ecosystems, being linked to a particular effect on the environment
- **Exposure assessment** – estimation of the concentrations/doses to which human populations (i.e. workers, consumers and individuals exposed indirectly via the environment) or environmental compartments (aquatic environment, terrestrial environment and air) are or may be exposed
- **Dose–response assessment** – determination of the relationship between the magnitude of the exposure and the probability of occurrence of the effects
- **Risk characterization** – description of the nature and the magnitude of risk

There are several successive interactive stages by which an environmental risk assessment proceeds (Figure 1). Problem identification is the most important activity, describing the resources, which could be affected, and the possible consequences of the action.

2. Hazard Identification

Before beginning a risk assessment activity, the purpose and aim are established (i.e. problem formulation), but it may be useful to review these at the starting point of the hazard characterization step, sometimes being needed to redefine the initial scope, that often requires interaction with the risk managers to ensure that the changes do not affect the utility of the final results. The initiation of a hazard characterization requires a systematic planning stage to identify the context, purpose, scope and focus of the study to be carried out. A general flow diagram for hazard characterization can be drawn (Figure 2). Hazard characterizations are typically developed by compiling information from a variety of data sources, using a plethora of test protocols. An appreciation of the strengths and limitations of the various data sources is critical to selecting appropriate data for use, and to establishing the uncertainty associated with dose–response models that are developed from different data sets and test protocols.

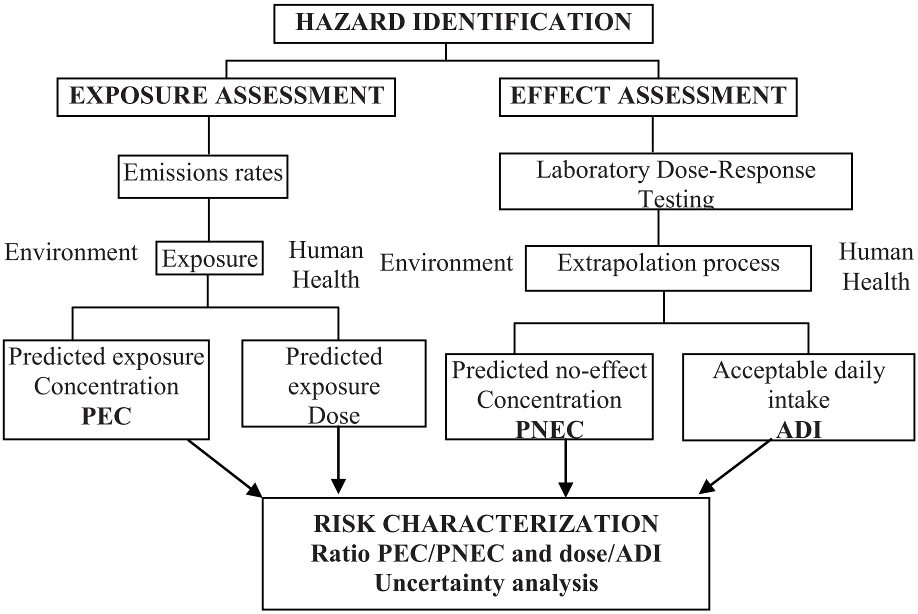

Figure 1. Framework of environmental risk assessment.

Active data collection is required, because reliance on passive data submission or data in published form does not usually provide enough information in sufficient detail to construct dose–response models. Relevant data come preferably from peer-reviewed journals. Given the current lack of data for hazard characterization, it is also advisable to evaluate the availability of unpublished, high-quality data sources.

2.1. CHEMICAL POLLUTANT CATEGORIES

Hazards (pollutants) can be clasified in physical, radiochemical, biological or chemical.

Considering the mixtures of chemical pollutants in the environment, the hazard will be characterised by the compounds identity, properties, concentrations and relationship between the components (eventually). There are two major categories of chemicals, organic and inorganic, organometallic chemicals being considered the third group.

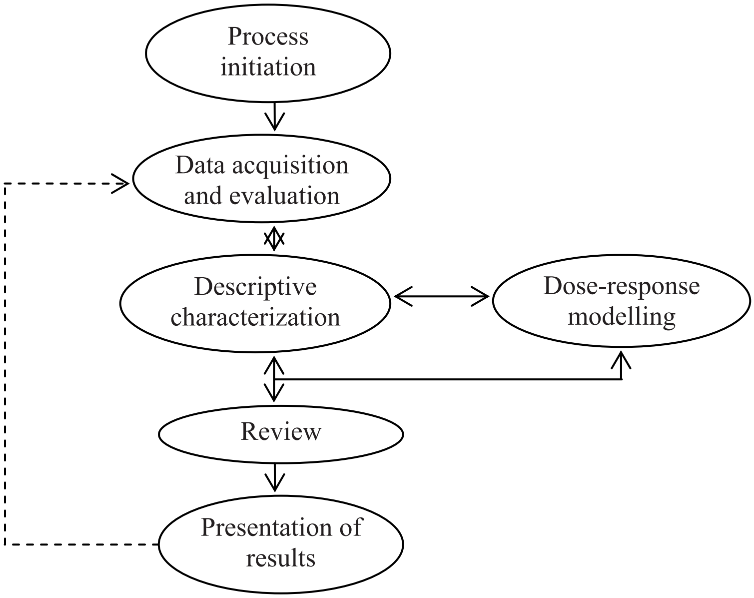

Figure 2. Schematic reprezentation of process flow for hazard characterization.

Inorganic pollutants are gases (SO_2, NO_x, CO, O_3), heavy metals (cadmium, lead, mercury, etc.) and nutrients or suspended particulate matter with particle diameter higher than 10 µm.

The main organic pollutants are volatile organic compounds (VOCs) (aliphatic and aromatic hydrocarbons, halogenated compounds, alcohols, aldehydes, esters, etc.), dioxins and furans, polychlorinated biphenyls (PCBs), pesticides and polycyclic aromatic hydrocarbons (PAHs). Mixtures of chemical pollutants in the environment contain either organic and/or inorganic pollutants, in gaseous, liquid or solid form. The following mixtures have been considered as very dangerous:

- Emissions from household combustion (coal and wood)
- Tobacco smoke
- Diesel engine and gasoline exhaust
- Welding fumes
- Asphalt fumes
- Mineral oils
- Creosotes
- Urban and industrial wastes
- Coal tars
- Polychlorinated and polybrominated biphenyls
- Bitumen, fuel oil residuals, gasoline

2.2. GENERAL CLASSIFICATION AND LABELLING REQUIREMENTS FOR DANGEROUS SUBSTANCES

Substances means *chemical elements or their compounds* in the natural state or obtained by any production process, *including any additive* necessary to preserve the stability of the product, *and any impurity* deriving from the production process used, *but excluding any solvent* which may be separated without affecting the stability of the substance or changing its composition. A substance may be chemically very well defined (e.g. acetone) or a complex mixture of constituents of variable composition (e.g. aromatic distillates). For certain complex substances, some individual constituents could be identified (REACH, 2006).

On the basis of physicochemical properties, substances can be: (i) Explosive, (ii) Oxidising, (iii) Extremely flammable, (iv) Other physical-chemical properties.

On the basis of toxicological properties, the classification of substances must be made considering the available experimental data according to with the following criteria which take into account the magnitude of these effects:

(a) For acute toxicity (lethal and irreversible effects after a single exposure)
(b) For subacute, subchronic or chronic toxicity
(c) For corrosive and irritant effects
(d) For sensitising effects
(e) For specific effects on health

The results of testing at a particular dose following the fixed dose method may be:

- Less than 100% survival
- 100% survival, but evident toxicity
- 100% survival, but no evident toxicity

The 2,000 mg/kg dose should be used primarily to obtain information on the toxic which could be: Very toxic (T+), Toxic (T), Harmful (Xn), Corrosive (C), Irritant (Xi).

On the basis of specific effects on human health pollutants can be: (i) Carcinogenic, (ii) Mutagenic, (iii) Toxic to reproduction.

On the basis of environmental effects, substances can affect aquatic or non-aquatic environment.

2.3. DESCRIPTION AND PROPERTIES OF CURRENT HAZARD SCREENING METHODS

Hazard screening can be comprehensive, intended to detect all potential hazards, or it can be more limited, detecting only a specific type of hazard. A comprehensive hazard assessment for a chemical substance generally requires a variety of in vitro and in vivo toxicological assays as well as evaluations of physical properties. The selection of individual screening tests depends on the setting and specific regulatory requirements. For example, the current practice of the U.S. Environmental Protection Agency (EPA) under the Toxic Substances Control Act (TSCA), in the absence of more extensive pre-existing data, is to screen new chemicals based solely on physicochemical data using quantitative structure – activity relationship models (National Research Council, 2007). In this setting, chemical tests may be limited to properties such as boiling point, octanol-water partition coefficient, vapour pressure and solubility.

If environmental fate and transport of substances are not primary concerns, short-term in vivo rodent assays may be used, such as a 28 day feeding study, which examines histopathology in most critical target organs. More comprehensive screening programs have adopted groups of tests that provide information on different types of toxicity but remain insufficient to fully assess chemical risks.

For example, the Organization of Economic Cooperation and Development (OECD) have developed the Screening Information Data Set (SIDS), which consists of the 21 data elements:

Physical-chemical properties – melting point, boiling point, relative density, vapor pressure, partition coefficient n-octanol/water, water solubility, dissociation constant, oxidation-reduction potential

Environmental fate – photodegradation, stability in water, transport and distribution between environmental compartments including distribution pathways, aerobic biodegradability

Environmental toxicology – acute toxicity to fish, acute toxicity to Daphnia, toxicity to algae, chronic toxicity, terrestrial toxicity

Mammalian toxicology – acute toxicity, repeated dose toxicity, genetic toxicity, reproductive toxicity, experiences with human exposure

Each toxicity test involves administrating a measured amount of a compound to the whole organisms, or to cells in culture, followed by measuring indicators of toxic outcomes.

Compared with more extensive tests, screening tests tend to use higher and fewer doses of the compound being studied, fewer test subjects, a shorter time period of observation, and less extensive evaluation of the toxic outcomes.

To reduce the use of mammals for laboratory testing, there is a strong impetus to develop and validate screening tests that use cultured cells or lower order animals, such as worms. The incorporation of toxicogenomics into screening tests involves measuring gene, protein, or metabolite changes in response to specific doses of an administered test compound at specific time points, with or without the parallel measurement of more traditional markers of toxicity. The critical question about new toxicogenomic techniques is whether they can improve hazard screening by making tests faster, more comprehensive, less reliant on higher order animals, and more predictive and accurate without being prohibitively expensive.

A critical challenge in designing and validating toxicogenomic screening tests is to identify and define a "gold standard" for hazard screening – the indication of the true state of toxicity against which the sensitivity and specificity of the screening test can be measured.

3. Exposure and Dose–Response Assessment

The exposure assessment has the objective to estimate the magnitude of actual and potential receptor exposures to environmental contaminants, the frequency and duration of these exposures, the nature and size of the populations potentially at risk (i.e., the risk group) and the pathways by which the risk group are or may be exposed.

3.1. DOSE AND CONCENTRATION RESPONSE

Anything can be toxic if the dose is high enough. The fate of a particular chemical after its entrance to the system depends on a number of factors, including:

- Physicochemical properties of the substance
- Physical, chemical and biological properties of the (eco)system
- Origin, amount, chemical form and fate of the substance in the environment

When establishing the relationship between dose and response, it is important to distinguish between the concentration of a chemical in the environment and the actual amount that reaches the target (human been or biota).

Low toxic is a chemical that, compared to other chemical, is usually measured by noting the lethal dose to half of the animals exposed to it (LD_{50}). The traditional lethally tests in which the LD_{50} is determined, are now replaced with one in which the animals are exposed simply to particular doses in order to classify the compound and to determine its toxicity rather than the lethal dose.

The LD_{50} may still have a limited use in the design and description of pesticides. Furthermore, it does not provide good information about the expression of the chemical's effect. The toxic potency of the chemical can be expressed also by LC_{50} which is defined as a concentration, at which 50% mortality of the organisms occur and by IC_{50} which is defined as the concentration at which 50% of growth or activity is inhibited.

The objective of the exposure assessment shall be to make a quantitative or qualitative estimate of the dose/concentration of the substance to which humans and the environment are or may be exposed. The assessment shall consider all stages of the life-cycle of the substance resulting from the manufacture and identified uses and shall cover any exposures that may relate to the hazards identified. The exposure assessment shall entail two steps: (i) generation of exposure scenario(s) or the generation of relevant use and exposure categories and (ii) exposure estimation, which shall be clearly identified as such in the Chemical Safety Report.

3.2. DEVELOPMENT OF EXPOSURE SCENARIOS

An exposure scenario includes, where relevant, a description of operational conditions, risk management measures and exposure estimation.

The operational conditions describe the current situation of the activity of concern like:

- Processes involved, including the physical form in which the substance is manufactured, processed and/or used
- Activities of workers related to the processes and the duration and frequency of their exposure to the substance
- Activities of consumers and the duration and frequency of their exposure to the substance
- Duration and frequency of emissions of the substance to the different environmental compartments and sewage treatment systems and the dilution in the receiving environmental compartment

The risk management measures included in the exposure scenarios are:

- Risk management measures to reduce or avoid direct and indirect exposure of humans (including workers and consumers) and the different environmental compartments to the substance
- Waste management measures to reduce or avoid exposure of humans and the environment to the substance during waste disposal and/or recycling

3.3. EXPOSURE ESTIMATION

The exposure estimation entails three elements: (1) emission estimation; (2) assessment of chemical fate and pathways; and (3) estimation of exposure levels.

The emission estimation shall consider the emissions during all relevant parts of the life-cycle of the substance resulting from the manufacture and each of the identified uses. The life-cycle stages resulting from the manufacture of the substance cover, where relevant, the waste stage. The emission estimation shall be performed under the assumption that the risk management measures and operational conditions described in the exposure scenario have been implemented.

A characterisation of possible degradation, transformation, or reaction processes and an estimation of environmental distribution and fate shall be performed (Mohapl, 2004; Valsaraj and Constanta, 2004).

An estimation of the exposure levels shall be performed for all human populations (workers, consumers and humans liable to exposure indirectly via the environment) and environmental spheres for which exposure to the substance is known or reasonably foreseeable. Each relevant route of human exposure (inhalation, oral, dermal and combined through all relevant routes and sources of exposure) shall be addressed (Fenner-Crisp, 2003). Such estimations shall take account of spatial and temporal variations in the exposure pattern. In particular, the exposure estimation shall take account of:

- Adequately measured, representative exposure data
- Any major impurities and additives in the substance
- The quantity in which the substance is produced and/or imported
- The quantity for each identified use
- Implemented or recommended risk management, including the degree of containment
- Duration and frequency of exposure according to the operational conditions
- The activities of workers related to the processes and the duration and frequency of their exposure to the substance
- The activities of consumers and the duration and frequency of their exposure to the substance
- The duration and frequency of emissions of the substance to the different environmental compartments and the dilution in the receiving environmental compartment
- The physicochemical properties of the substance
- Transformation and/or degradation products
- The likely routes of exposure of and potential for absorption in humans
- The likely pathways to the environment and environmental distribution and degradation and/or transformation scale (geographical) of exposure
- Matrix dependent release/migration of the substance

Where adequately measured representative exposure data are available, special consideration shall be given to them when conducting the exposure assessment.

Appropriate models can be used for the estimation of exposure levels. Relevant monitoring data from substances with analogous use and exposure patterns or analogous properties can also be considered.

4. Risk Characterisation

The risk characterisation shall be carried out for each exposure scenario and shall be presented under the relevant heading of the Chemical Safety Report.

The risk characterisation shall consider the human populations and the environmental spheres for which the estimation of exposure levels has been done, under the assumption that the risk management measures described in the exposure scenarios have been implemented. In addition, the overall environmental risk caused by the substance shall be reviewed by integrating the results for the overall releases, emissions and losses from all sources to all environmental compartments.

The risk characterisation consists of:

- A comparison of the exposure of each human population known to be or likely to be exposed with the appropriate derived no-effect level (DNEL)
- A comparison of the predicted environmental concentrations in each environmental sphere with the predicted no-effect concentrations (PNEC)
- An assessment of the likelihood and severity of an event occurring due to the physicochemical properties of the substance

For any exposure scenario, the risk to humans and the environment can be considered to be adequately controlled, throughout the lifecycle of the substance that results from manufacture or identified uses, if:

- The exposure levels estimated do not exceed the appropriate DNEL or the PNEC.
- The likelihood and severity of an event occurring due to the physicochemical properties of the substance is negligible.

For those human effects and those environmental spheres for which it was not possible to determine a DNEL or a PNEC, a qualitative assessment of the likelihood that effects are avoided when implementing the exposure scenario shall be carried out.

4.1. CRITERIA FOR THE IDENTIFICATION OF DANGEROUS SUBSTANCES

Persistent, Bioaccumulative and Toxic substances (PBTs) as well as Very Persistent and Very Bioaccumulative substances (vPvBs) are generally considered to be substances of very high concern (Tyle et al., 2002).

4.1.1. *Bioaccumulative and Toxic Substances*

A substance that fulfils all three of the criteria of the sections below is a persistent, bioaccumulative and toxic (PBT) substance.

Persistence. A substance fulfils the persistence criterion (P) when the half-life in marine water is higher than 60 days, or the half-life in fresh- or estuarine water is higher than 40 days, or the half-life in marine sediment is higher than 180 days, or the half-life in fresh- or estuarine water sediment is higher than 120 days, or the half-life in soil is higher than 120 days. The assessment of the persistency in the environment shall be based on available half-life data collected under the adequate conditions, which shall be described by the registrant.

Bioaccumulation. A substance fulfils the bioaccumulation criterion (B) when the bioconcentration factor (BCF) is higher than 2,000. BCF is calculated as the ratio between the metal concentration in biota and in water. The assessment of bioaccumulation shall be based on measured data on bioconcentration in aquatic species. Data from freshwater as well as marine water species can be used.

Toxicity. A substance fulfils the toxicity criterion (T) when the long-term no-observed effect concentration (NOEC) for marine or freshwater organisms is less than 0.01 mg/L, or the substance is classified as carcinogenic (category 1 or 2), mutagenic (category 1 or 2), or toxic for reproduction (category 1, 2, or 3), or there is other evidence of chronic toxicity, as identified by the classifications: T, R48 (Danger of serious damage to health by prolonged exposure) or Xn, R48 according to Directive 67/548/EEC (EC, 2001).

4.1.2. *Very Persistent and Very Bioaccumulative Substances*

A substance that fulfils the criteria of the sections below is a very persistent and very bioaccumulative (vPvB) substance.

Persistence. A substance fulfils the very persistence criterion (vP) when (i) the half-life in marine, fresh- or estuarine water is higher than 60 days, or (ii) the half-life in marine, fresh- or estuarine water sediment is higher than 180 days, or (iii) the half-life in soil is higher than 180.

Bioaccumulation. A substance fulfils the very bioaccumulative criterion (vB) when the bioconcentration factor is greater than 5,000.

5. Metal Concentration Factors in Marine Ecosystem – Case Study

The aim of the performed studies in 2003–2006 period was to assess the environment exposure to trace metals (cadmium, chromium, copper, lead, nickel and silver) in the south of the Romanian Black Sea coast ecosystem by the determination of bioconcentration factors (BCF) in algae, shells, shrimps and two kinds of fishes.

Cadmium, chromium, copper, lead, nickel and silver play an important role in marine ecosystems as pollutants or essential elements, suffering migrations described as biogeochemical cycles. The involved processes in biogeochemical cycles of metals are adsorption/precipitation versus solubilisation in water/sediments equilibrium or degradation versus bioaccumulation in biota/biotope equilibrium. Another occurring process is the biomagnification when the pollutant concentration is amplified on the trophic chain by feed (Chirila et al., 1999; Chirila and Draghici, 2003; Chirila, 2004; Chirila et al., 2004).

5.1. EXPERIMENTAL DESIGN

The following samples have been collected in August 2003, 2004, 2005 and February 2006 from Mangalia Golf, located in the southern part of the Romanian Black Sea coast: fresh water, alga (*Ulva sp.*), shells (*Mytillus sp.*), shrimps (*Crangon sp.*), hanos fish (*Ponticola sp.*), and anchovy fish (*Encrasicholus sp.*).

The biota samples have been carefully prepared for analysis: washed with distilled water, dried at 105°C, mortared and then dissolved with Digesdahl device Hach by adding 65% nitric acid and hydrogen peroxide. The applied analytical method was inductive coupled plasma-mass spectrometry using an ICP-MS Agilent 7500a device (Petisleam et al., 2005). Average bioconcentration factor has been calculated and graphically represented.

5.2. RESULTS AND DISCUSSIONS

The 4 years average values of bioconcentration factors show a minimum for silver, followed by chromium, lead, copper, cadmium and nickel (Table 1).

TABLE 1. Bioconcentration factors of metals in marine ecosystem (average values for the 5 years).

Sample/metal	Ag	Cd	Cr	Cu	Pb	Ni
Alga	53	206	217	166	222	610
Shrimps	166	236	264	1,092	157	930
Shells	160	1,175	141	260	466	1,750
Anchovy	97	294	178	130	170	352
Hanos	75	334	131	131	154	298

There is a large variation of concentration factors in each biota category, that may depend on the sample collecting points, the species and physiological behaviour of the organisms (Figures 3, 4, 5, 6, and 7). In alga the annual BCF values vary from 25 to 1,389, in shrimps from 75 to 3,857, in shells from 37 to 4,768, and in fishes from 25 to 814.

Figure 3 shows that in alga *Ulva sp* Ni cations have the highest bioaccumulation in 2003 and 2004, but did not exceeded the bioaccumulation accepted level (2,000).

Figure 4 presents the BCF in shells *Mytillus sp*., showing that two of the heavy metal cations have exceeded the BCF accepted value Cd (in 2003) and Ni (in 2005). Lead also has high bioconcentration factor but in accepted limits. Moreover, Ni BCF value in 2005 is close to the very bioaccumulative (vB) limits (5,000).

The BCF evaluated in shrimps *Crangon sp.* (Figure 5) also presents Ni exceeding the 2,000 limit (and also in 2005) but Cu has registered higher BCF values in 2004.

The bioaccumulation factors registered for the two studied fishes (anchovy *Encrasicholus sp. and* hanos *Ponticola sp.*) are presented in Figures 6 and 7 and registered some similar results. Cd and Ni cations have higher BCF values that the other cations, Cd in 2005 and Ni in 2004 (for both fishes) and Ni also in 2005, for anchovy.

The measured concentration factors show comparable values with other reported data (Griscom et al., 2002; Guhathakurta and Kaviraj, 2000; Kut et al., 2000; Pantelică et al., 2005; Storelli et al., 2001; Topcuoglu et al., 2003; Topcuoglu et al., 2004).

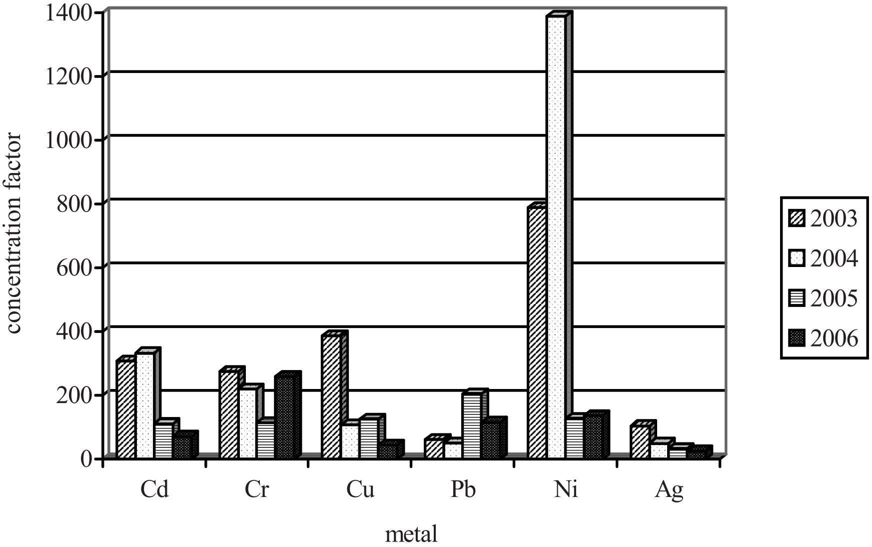

Figure 3. Metal bioconcentration factors dynamics in alga *Ulva sp.* from the Black Sea coast in 2003–2006.

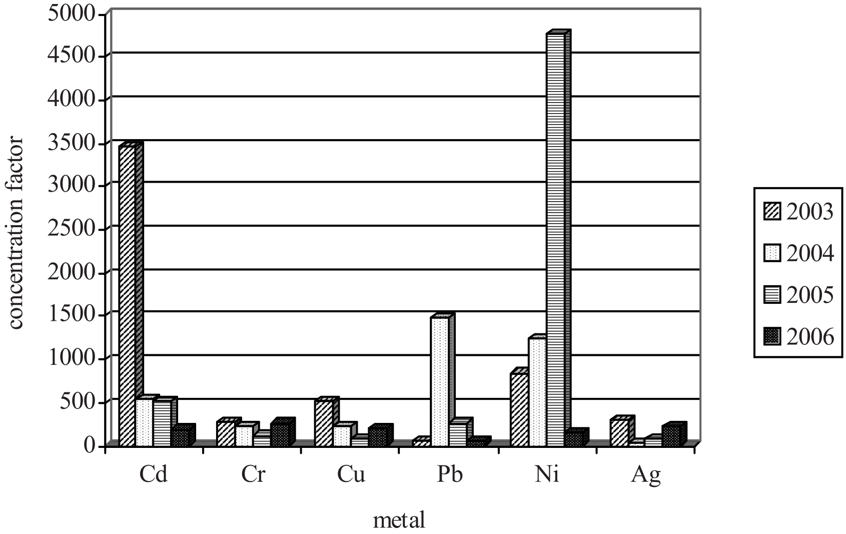

Figure 4. Metal bioconcentration factors dynamics in shells *Mytillus sp*. from the Black Sea coast in 2003–2006.

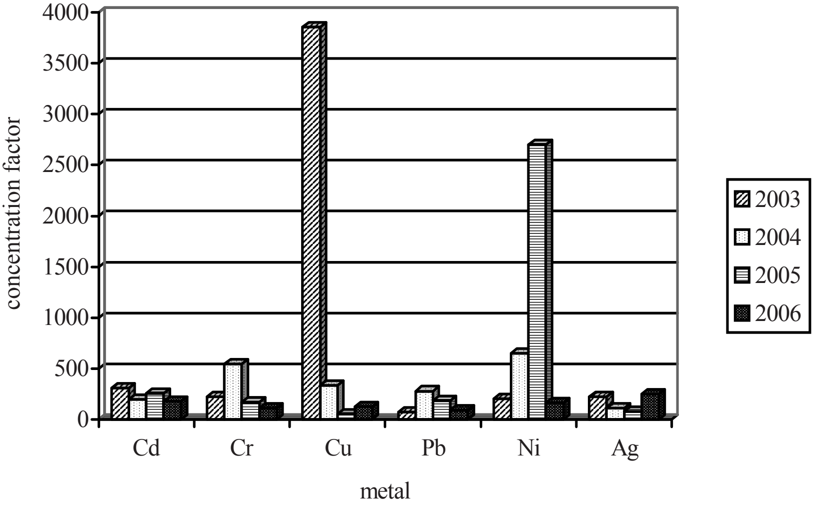

Figure 5. Metal bioconcentration factors dynamics in shrimps *Crangon sp.* from the Black Sea coast in 2003–2006.

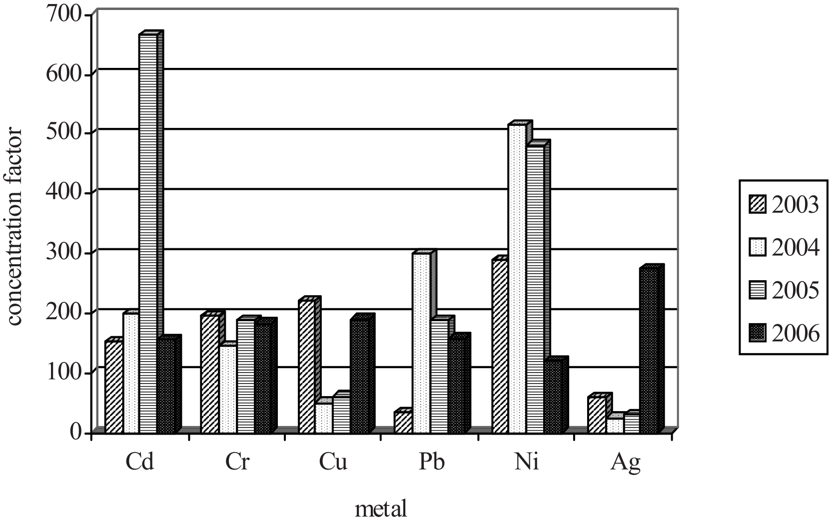

Figure 6. Metal bioconcentration factors dynamics in anchovy (*Encrasicholus sp.*) from the Black Sea coast in 2003–2006.

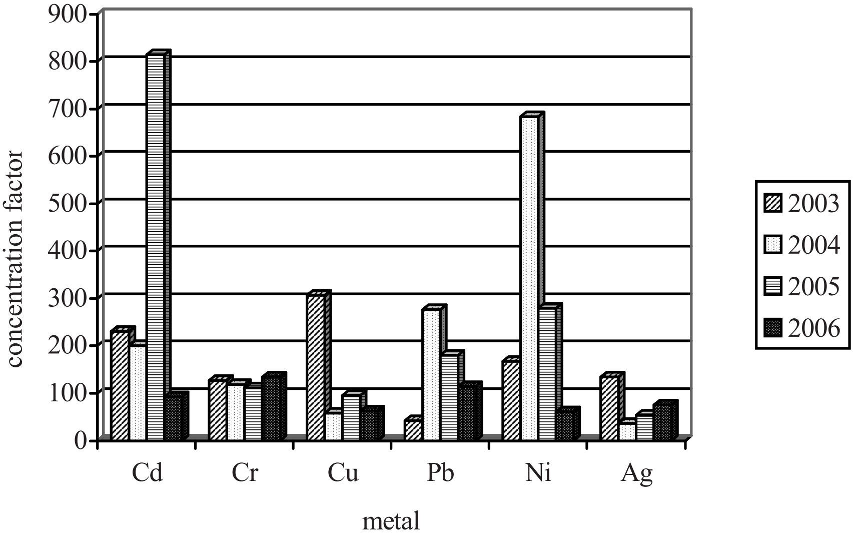

Figure 7. Metal bioconcentration factors dynamics in hanos (*Ponticola sp.*) from the Black Sea coast in 2003–2006.

6. Conclusions

This paper presented an overview of the risk assessment activity with emphasis on the approach of the mixtures of chemical pollutants in the environment. The theoretic presentation is completed with a case study of bioconcentration factors determination for six heavy metals (cadmium, chromium, copper, lead, nickel and silver) in the Romanian Black Sea water and marine biota, during 2003–2006.

The results demonstrated that the highest bioavailability for heavy metals is registered by shells (*Mytillus sp.*) and shrimps (*Crangon sp.*) and the most bioaccumulated metals are Cu, Cd and Ni. Moreover, Ni is close to the very bioaccumulative limits in 2005, in shells. The reported BCF allow concluding that at the moment there is no pollution concern in the studied area.

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MASS BALANCE MODELS FOR CHEMICAL FATE, BIOACCUMULATION, EXPOSURE AND RISK ASSESSMENT

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Abstract. National and international regulatory programs seek to evaluate the potential hazards and risks of commercial chemicals to humans and the environment. There are relatively few measured laboratory and field based monitoring data available for the mandated assessments, thereby requiring the use of Quantitative Structure-Activity Relationships (QSARs) and mass balance models. The present study reviews mass balance models that are available to estimate chemical fate, transport and distribution in the physical environment, bioaccumulation in food webs and exposures and risks to ecological receptors and humans. The focus is on the assessment of organic chemicals using evaluative models.

Keywords: mass balance models, fate and transport, bioaccumulation, exposure assessment, risk assessment

1. Introduction

National and international regulatory programs and treaties seek to evaluate the hazards and risks that commercial chemicals may pose to humans and the environment (U.S. EPA, 1976; Government of Canada, 1999; UNEP, 2001; European Commission, 2001). Globally, there may be as many as 100,000 existing chemicals and approximately 1,000–2,000 new chemicals added annually that require assessment (Muir and Howard, 2006). Unfortunately, there are few measured laboratory data (e.g., chemical properties and toxicity information) and few environmental monitoring data available for these assessments

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L.I. Simeonov and M.A. Hassanien (eds.), *Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology*,

(Muir and Howard, 2006; Arnot and Gobas, 2006). Moreover, there are insufficient resources (time, money, people and equipment) to collect and analyze a sufficient number of samples to accurately understand the complex relationships between emissions and the exposure of humans and ecosystems for all chemicals. The reality of this situation necessitates the use of Quantitative Structure-Activity Relationships (QSARs) and mass balance models to estimate chemical hazards and risks at least for preliminary assessments so that the limited resources can focus on those chemicals that pose the greatest concerns.

The objective of this paper is to review computational models for environmental fate, bioaccumulation, exposure and risk assessment with a focus on mass balance modelling. Basic elements and concepts of models, in particular mass balance models, are first introduced. An overview of different types of models that can be used to assess the environmental fate, bioaccumulation, exposure and risk assessment of organic chemicals is presented. Finally, the limitations of models and future research needs are outlined.

2. Models

There are many types of models (e.g., conceptual, statistical, mass balance) used in a variety of environmental and human health applications and for various purposes. The United States National Research Council (NRC, 2007) defines a model as:

> *A simplification of reality that is constructed to gain insights into select attributes of a particular physical, biological, economic, or social system.*

Models are necessarily based on simplifying assumptions and cannot be expected to replicate the inherent complexity of actual systems. While recognizing these limitations it is also realized that models are essential for a variety of purposes in various scientific disciplines. Models are used to analyze data and processes and can be used to predict future outcomes based on previous knowledge. These predictions are essentially “working hypotheses” that can usually be tested with measured data. Model development, evaluation (sometimes termed validation), refinement, and application are therefore key elements in the evolutionary scientific process towards improved understanding. Models cannot provide “truths” or make decisions; however, they can be used to inform decisions, particularly if they are designed for a specific purpose. It must be recognized that measurements are also limited for regulatory decision-making because they are usually incomplete and often variable and uncertain. A strategy for improving environmental and human health assessments is to combine both models and measurements (McKone et al., 2007). Further detailed discussions on models, particularly for chemical regulatory purposes, are provided elsewhere (Webster et al., 2005; CREM, 2008; Mackay, 2001). Other than addressing regulatory needs, mass balance models are also valuable research and educational tools for exploring and teaching new scientific concepts including the behavior of chemicals in physical and biological systems.

The following discussion concentrates on mass balance modelling for organic chemical evaluations. Mass balance modelling concepts are first briefly described followed by specific discussions and examples of mass balance models for fate and transport, bioaccumulation, exposure and risk assessment.

3. Basic Mass Balance Modeling Concepts

Mass balance multi-compartment models pioneered by Mackay are the most commonly used models to quantify the fate, transport and transformation of organic chemicals in the environment (McKone and MacLeod, 2003). These models use mathematical expressions to combine chemical transport processes (e.g., diffusion in water and advection by wind) and chemical transformation processes (e.g., microbial degradation, hydrolysis) with thermodynamic principles to quantify chemical fate, transport and behavior. The models are grounded in laws for the conservation of mass and energy. The fugacity concept has proven particularly useful in the development of environmental mass balance models (Mackay, 2001). In particular, the fugacity approach facilitates development of the mass balance equations and the results are more readily interpreted. For example, since fugacity is an equilibrium criterion analogous to chemical potential, the equilibrium status of the system can be readily assessed. Interested readers are encouraged to further explore the details of these models and the fugacity concept (Mackay, 2001).

In a simplistic sense the biosphere is comprised of a multitude of interconnected compartments and phases of various composition and size. Examples include the atmosphere, water bodies, bottom sediment, soil, biological organisms, tissues and cells. These compartments and phases can be viewed as a series of “boxes” in which chemicals can exist either in a fixed state, pass through or be in the process of transformation or reaction. In the environment most of these compartments are heterogeneous in nature (e.g., sediments and soils); however, some are relatively well-mixed phases (e.g., ponds). Properties such as volume, density and composition of each compartment in the mass balance equation must be defined. A single phase (e.g., air) can be modeled as a single box or as a number of boxes thus providing greater spatial resolution for the total air compartment. Representing heterogeneous concentrations in mass balance models can be difficult resulting in complex and parameter-intensive models; therefore, a typical simplifying assumption for model development is that concentrations in a particular box are homogeneously distributed. This is often referred to as the Continuous Stirred Tank Reactor (CSTR) assumption.

Spatially, mass balance equations link the transport of chemical into and out of the various compartments (e.g., from air to water or water into a fish) and quantify processes within these compartments (e.g., reaction or formation). The model equations can be derived and solved as a function of time or at steady state. Steady state reflects a situation in which the chemical concentrations no longer change as a function of time, i.e., chemical input quantities equal chemical "loss" or output quantities. The steady state assumption is often used because it simplifies the mathematical and computational requirements to solve the equations. Steady state solutions (which are algebraic in nature) can also more clearly identify key processes and parameters that describe and influence chemical behavior in the system. It is recognized that complex environmental systems are never truly at steady state; however, in certain cases "pseudo-steady state" conditions can be observed. Commercial chemicals released to the environment continuously or semi-continuously over years of production and use may approximate "pseudo-steady state" conditions at least in regions where they are discharged. When conditions are changing with time it is necessary to compile and solve the differential equation for each box, i.e., the inventory change is equated to the difference between the input and output rates (Mackay, 2001). Usually these equations are solved numerically, but in simple cases an analytical solution can be obtained.

The second law of thermodynamics determines that in a system comprised of different phases such as the natural environment, chemical molecules migrate from phase to phase "seeking" a minimal Gibbs free energy for the system, i.e., equilibrium (Mackay, 2001). Chemicals diffuse from high to low chemical potential (or fugacity); however, there are also inter-media transport processes that affect the distribution of chemical in natural systems (e.g., rain moves chemical from the air into soils and lakes). Mass balance models can provide insights into the equilibrium status between the compartments of the defined system. This information is valuable because it shows why and how chemicals move from one phase to another. For example, the process of food web biomagnification results in chemical potentials (or fugacities) that can be higher in predators than in their diet (Connolly and Pedersen, 1988). The rates of inter-media chemical transfer can also be obtained and interpreted. As discussed below, simpler fate models assume equilibrium conditions between environmental phases and more complex models account for inter-media chemical transport.

Models can be developed, parameterized and applied to specific conditions with a view to describing an actual environment or situation. Real environments are highly complex and models developed for site-specific applications can be resource intensive and limited to a particular site or application. Alternatively, models can also be developed and applied in an evaluative sense in which the system is parameterized to be representative of general environmental conditions. Models should be developed based on a particular objective. Each increase in model complexity typically results in more mathematical complexity, the need for more data to parameterize the model, and more time required to interpret the model results. Furthermore, complex models may also deter consensus, which is a necessary facet for regulatory acceptance. Evaluative models are particularly useful for comparing and prioritizing lists of chemicals for exposure and risk assessments because they provide a consistent framework such that the results are determined by the unique characteristics of the chemical (partitioning properties, half-lives, emission rate, toxicity).

4. Mass Balance Model Input Requirements

All mass balance models require some information for chemical properties such as vapor pressure, water solubility, and octanol-water partition coefficient (K_{OW}), and for reactivity (usually first order rate constants or half-lives) in a variety of media (e.g., atmosphere, fish). Data requirements typically increase with more complex models. The accuracy of the required input data is vital to obtain accurate model results ("garbage in = garbage out"). Handbooks and databases containing measured or recommended property values (Mackay et al., 2000; Howard et al., 1991; Arnot and Gobas, 2006) and toxicity data are available (e.g., www.cfpub.epa.gov/ecotox/); however, these data are mostly limited to "well-studied" chemicals. There is thus an urgent need to develop reliable QSARs that can estimate these properties from chemical structure. Considerable progress has been made, but a significant amount of research remains to improve existing models, especially for more complex molecules and those with less common functional groups. A coordinated program of laboratory based property determination and QSAR development is needed to improve chemical exposure and risk assessments. The mass balance models can be used to conduct sensitivity and uncertainty analyses for chemical input parameters to direct priorities for accurate input data requirements (MacLeod et al., 2002).

In summary, mass balance models range in complexity according to the data available to develop, parameterize, apply and evaluate the model, the purpose of the model, and the time and money committed to that purpose. Environmental mass balance models can be broadly categorized according to the processes they describe, namely (i) fate and transport, (ii) single organism and food web bioaccumulation, and (iii) multimedia exposure and risk assessment. These three model categories are reviewed below.

5. Mass Balance Fate and Transport Models

Mass balance fate and transport models vary in complexity (e.g., Levels I–IV), purpose (e.g., evaluative and "real-world"), and scale, (e.g., local, regional, continental and global) (Cowan et al., 1995; Mackay, 2001; McKone and MacLeod, 2003). These models can be used to simulate chemical distribution in multiple environmental phases within a specified region, residence times in a particular compartment or a region, transport from one region to another region, and persistence in the environment. Notably, chemical persistence in the environment is related to chemical exposure potential (MacLeod and McKone, 2004) and is thus an obvious parameter for chemical regulatory objectives. If actual emission rates are known the models can also calculate expected chemical concentrations in different environmental media such as air, water, sediment and soil. Simpler models are first described followed by more complex models.

Level I model calculations simulate the simple situation in which a chemical achieves equilibrium between a number of different phases of defined composition and volume. For example, the equilibrium distribution of a chemical in an evaluative environment comprised of defined air, aerosol, water, soil, sediment, suspended sediments, and fish compartments. The characteristics of these environmental compartments can represent general environmental conditions such as phase volumes and densities and fractions of organic matter in the various phases. A Level I model assumes no degradation or reaction and no advection into or out of the defined environment.

Level I model calculations require only basic chemical properties (e.g., molar mass, water solubility, vapor pressure and K_{OW}). The compartment receiving the emission is unimportant because of the equilibrium assumption. Level I models provide preliminary information as to where a chemical is likely to partition based on the defined environmental characteristics and the properties of the chemical; however, the simplifying assumptions can be misleading for comparative chemical assessments.

Level II model calculations simulate a situation in which a chemical is released into an environment at a constant rate assuming steady state and inter-compartmental equilibrium conditions. Level II models introduce rates of chemical reaction (degradation) in the defined environmental compartments and "in flow" and "out flow" (advection in water and air); therefore, Level II models simulate some naturally occurring processes that are not included in Level I calculations. Inter-media transport processes (e.g. wet deposition, or sedimentation) are not quantified in a Level II calculation and chemical quantities put into the system equal chemical "loss" or output quantities from the system, i.e., steady state. The compartment receiving the emission is unimportant because of the equilibrium assumption.

Level II model calculations require basic chemical property information (e.g., molar mass, water solubility, vapor pressure and K_{OW}) and reaction half-lives for the different compartments. The chemical distribution in the defined environmental compartments thus reflects the partitioning properties, degradation properties, advection rate information and environmental properties. The model shows which chemical "loss" processes are expected to be relevant in the environment. It is noteworthy that a fast reaction or short half-life in a particular compartment (e.g., air) may not be significant if relatively little chemical is subject to this reaction as a result of its environmental distribution.

Figure 1 shows a Level II model calculation for carbon tetrachloride based on an assumed emission rate of 1 kg/h. Instantaneous equilibrium between all compartments of the model is assumed for the Level II calculations, thus the fugacities are equal; however, the concentrations and mass quantities in each compartment are highly variable. Not surprisingly, this volatile chemical largely partitions to air (>99%). Carbon tetrachloride is rather persistent in the environment as indicated by the reaction residence time of more than 24,000 h. Most of the carbon tetrachloride that enters the system is eliminated by advection in air (>99%). It is important to recognize that while it is "lost" or blown away from this regional environment it is "gained" by neighboring regions. The advection residence time is only 100 h and thus advection is the dominant contribution to the overall residence time of 99.8 h.

Level III model calculations are more complex and realistic than Level II calculations. As with the Level II model, chemical is discharged at a constant rate and achieves a steady state condition in which input and output rates are equal. The loss processes in Level III models also include degrading reactions and advection. Level III models introduce inter-compartmental transfer rates, thus equilibrium between multimedia compartments (e.g., air and water) no longer applies. The Level III environment is becoming more representative of the real world by including inter-media transfer processes such as wet deposition (rain).

Level III model calculations require the same basic chemical property and reaction half-life information as Level II models; however, Level III models also require the user to specify the chemical's mode-of-entry to the environment, i.e., to air, or water, or soil, or some combination of these media. The chemical distribution in the defined environmental compartments thus reflects the partitioning properties, inter-media transfer processes, degradation properties, advection rate information, and environmental properties. Valuable insights obtained from Level II and Level III models include those of overall chemical persistence or residence time and potential for long-range transport in air or water.

Figure 1 shows a Level III model calculation for *p,p'*-DDT based on an assumed emission rate of 1 kg/h. For this illustrative simulation it was assumed that emissions were equal to air, water and soil. The fugacities are not equal in the various compartments and sediments are at a higher fugacity than the other compartments. This reflects in part the partitioning properties of the chemical and the inter-media transport of particle sedimentation from the water column. The concentrations and mass quantities in each compartment are highly variable and there is a substantial concentration in sediment and a significant quantity in soil. Not surprisingly, this non-volatile, hydrophobic chemical largely partitions to soil and sediment. *p,p'*-DDT is persistent in the environment as indicated by the reaction residence time of more than 28,000 h. At steady state, reaction in soil is the highest loss process (0.48 kg/h). The advection residence time is more than 48,000 h.

Level IV models introduce the capacity to model changes in chemical behavior as a function of time. The steady state assumption no longer applies. This involves the solution of differential mass balance equations to describe the time dependent or dynamic behavior of chemicals released to the environment. Level IV model calculations can still reach steady state or “pseudo-steady state” conditions.

As shown in Figure 1, significant quantities of chemical can move from “source” regions in which the chemical is released to “remote” regions. These advective transport phenomena place an unfair burden on regions receiving chemicals where they were not used. Long-range transport (LRT) is an important trans-boundary topic and ethical issue. The United Nations Stockholm Convention on Persistent Organic Pollutants (UNEP, 2001) addresses the issue by regulating 12 substances or groups of substances that have been demonstrated to undergo LRT. There are certain to be more chemicals identified in the future for international regulatory action. Monitoring data in remote regions provides the most compelling evidence that significant LRT has occurred; however, accounting for which region contributes what quantity to the global distribution pattern can only be determined using mass balance models. Mass balance models demonstrate that monitoring data are consistent with our present understanding of LRT processes. Models can be used to identify chemicals with LRT potential and provide estimates of the fraction of the mass of chemical released in one location that may reach a distant region as well as the rate of transport (Wania, 2003; Wegmann et al., 2009; Mackay and Reid, 2008).

Table 1 lists a selection of fate and transport models that have been applied to evaluative and real environments. Free downloads and further descriptions of these models or links to these models are available at the Canadian Centre for Environmental Modelling and Chemistry (CEMC) website www.trentu.ca/cemc.

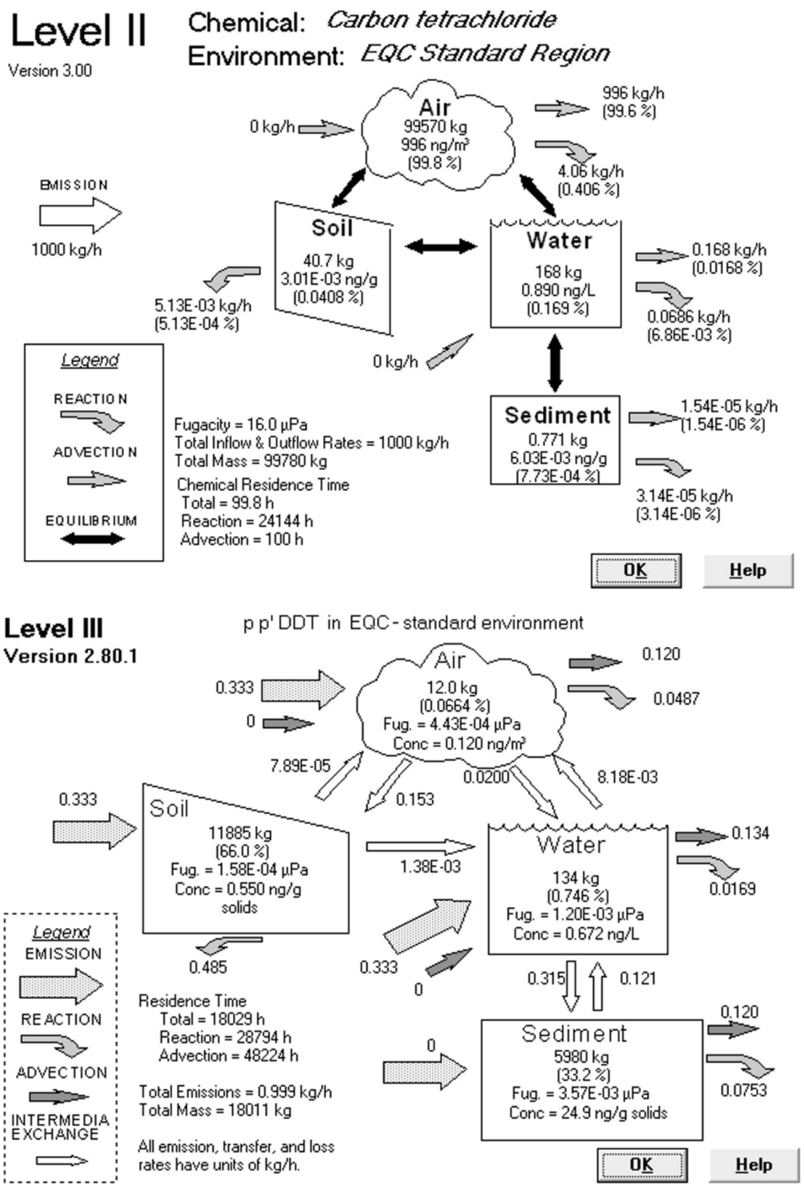

Figure 1. An illustration of The Canadian Centre for Environmental Modelling and Chemistry (CEMC) Level II (*upper*) and Level III (*lower*) evaluative fate and transport model calculations for carbon tetrachloride and p,p'-DDT, respectively. The simulations assume an emission rate of 1 kg/h to the regional environment. For the Level III model, emissions to the environment are assumed equal to air, water and soil.

TABLE 1. Mass balance fate and transport models for evaluative and real environments. Free downloads and descriptions of these models or links to these models are available from the website www.trentu.ca/cemc.

Model name	Description	Reference
Level I	Model for the equilibrium distribution of a fixed quantity of conserved chemical, in a closed environment	(Mackay, 2001)
Level II	Model for the equilibrium distribution of a non-conserved chemical discharged at a constant rate into an open environment at steady-state	(Mackay, 2001)
Level III	Model for the steady state distribution of a non-conserved chemical discharged at a constant rate into an open environment	(Mackay, 2001)
ChemCAN	Steady state model for 24 regions of Canada. It is easily applicable to other regions by the addition of regional properties	(Webster et al., 2004)
CoZMo-POP 2 Model	Dynamic model for the long-term fate of persistent organic pollutants in a coastal environment or a drainage basin of a large lake	(Wania et al., 2006)
BETR-North America	Regionally segmented multi-compartment, continental-scale model for North America	(MacLeod et al., 2001)
BETR-World	Regionally segmented multi-compartment, global-scale chemical fate model	(Toose et al., 2004)
BETR-Global	Global-scale multimedia contaminant fate model that represents the global environment as a connected set of 288 multimedia grids	(MacLeod et al., 2005)
GloboPOP	A Level IV multimedia model describing the global fate of persistent organic chemicals	(Wania, 2003)
The OECD Tool	Steady state model to screen chemicals for persistence and long-range transport potential	(Wegmann et al., 2009)

6. Mass Balance Bioaccumulation and Food Web Bioaccumulation Models

Bioaccumulation is the net result of competing rates of chemical uptake and elimination in an organism and can result in concentrations in organisms that are orders of magnitude greater than concentrations in the air or water in which they reside (Arnot and Gobas, 2006). Bioaccumulation includes uptake by respiration of chemical from the environment surrounding the organism (specifically referred to as bioconcentration) and dietary exposures. Major routes of chemical elimination include loss by respiration, fecal egestion, urinary excretion, metabolic biotransformation, growth dilution and reproductive transfers (e.g., lactation in mammals). Figure 2 illustrates major routes of chemical uptake and elimination in fish. Dietary exposures can result in biomagnification; an increase in chemical concentration with increasing trophic level. Significant metabolic biotransformation can result in biodilution; a decrease in chemical concentration with increasing trophic level. Biomagnification and biotransformation processes are chemical specific and thus result in orders of magnitude difference in exposures for chemicals with the same partitioning properties (e.g., K_{OW}) (Arnot and Gobas, 2006; Arnot et al., 2008). Two general approaches have been used to assess and predict bioaccumulation: relatively simple regression models or QSARs and more complex mechanistic models that simulate uptake and loss processes (Mackay and Fraser, 2000).

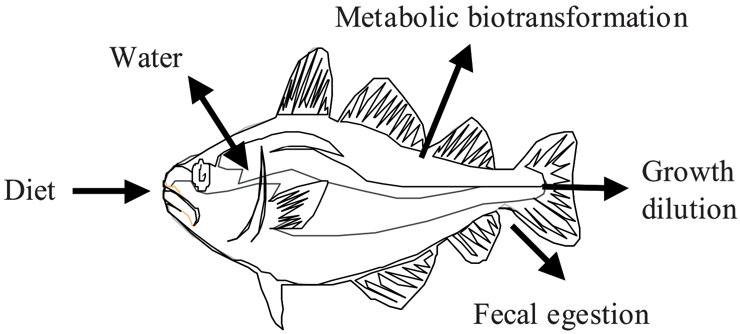

Figure 2. Major routes of chemical uptake and elimination in fish.

The majority of data and models currently used in regulatory programs to assess bioaccumulation (exposure potential) originate from studies in the aquatic environment. Bioaccumulation in aquatic systems is assessed using the bioconcentration factor (BCF) or the bioaccumulation factor (BAF). The BCF and BAF are both measured as ratios of the chemical concentration in the organism (e.g., fish) to the chemical concentration in the water at steady state. The BCF is measured under controlled laboratory conditions in which the organism is not exposed to chemical in its diet. The BAF is measured under field conditions in which the organism is exposed to chemical from the water and its diet. Notably, chemical bioaccumulation in water-respiring aquatic organisms is determined largely by the hydrophobicity (K_{OW}) of the chemical (Mackay, 1982) and its susceptibility to biotransformation (Arnot et al., 2008). In the absence of measured BCF and BAF data, chemicals are evaluated for bioaccumulation potential using QSAR and mass balance models. Model selection can have significant impacts on which chemicals are identified as bioaccumulative hazards and which ones are not considered to be hazardous

(Arnot and Gobas, 2006). Most BCF-QSAR models are K_{OW} based regressions, thus neglecting chemical specific properties (biomagnification and biotransformation potential) in bioaccumulation hazard assessments (Arnot and Gobas, 2006; Arnot et al., 2008).

There are fundamental differences in bioaccumulation potential for water-respiring and air-breathing organisms. Air-breathing organisms exchange chemical with the air; therefore, bioaccumulation potential is also determined by the octanol-air partition coefficient (K_{OA}) as well as K_{OW} and biotransformation capacity. From a scientific and regulatory perspective, there has been increasing attention in recent years to bioaccumulation potential in air-breathing organisms (Gobas et al., 2003; Kelly et al., 2007; Kelly and Gobas, 2001; Czub and McLachlan, 2004). In the absence of biotransformation approximately 60% of commercial chemicals currently being evaluated in global regulatory programs have the potential to be bioaccumulative hazards in air-breathing organisms that are not considered to be bioaccumulative hazards in water-respiring organisms (Gobas et al., 2003; Kelly et al., 2007; Kelly and Gobas, 2001; Czub and McLachlan, 2004). Thus, current regulatory criteria do not exist to explicitly identify bioaccumulative hazards in air-breathing organisms.

A widely used biotransfer factor (BTF) QSAR model developed by Travis and Arms is a K_{OW} based regression to estimate chemical concentrations in milk and beef in agricultural food chains for human exposure assessments (Travis and Arms, 1988). This treatment of bioaccumulation does not account for mechanistic principles in air-breathing organisms and does not account for chemical specific differences in exposure potential as a result of biomagnification and biotransformation processes. The use of simple K_{OW} based regression equations for BTFs implies that all chemicals with the same K_{OW} have the same BTF in agricultural food webs.

Mass balance BCF models originally developed to quantify chemical uptake and elimination in fish from laboratory data (e.g., Neely et al., 1974) have been refined to express the bioaccumulation processes in the environment using mechanistic mass balance models for a variety of species and food webs (Thomann, 1989; Barber et al., 1991; Gobas, 1993; Campfens and Mackay, 1997; Kelly and Gobas, 2003; Gobas et al., 2003; Arnot and Gobas, 2004). These mechanistic mass balance bioaccumulation models incorporate key uptake and elimination processes (e.g., respiration, diet, fecal egestion, metabolic biotransformation, and growth dilution). Moreover, these models include differences for the media that organisms respire (air or water) as well as physiological characteristics (e.g., body size, feeding rates, bioenergetics, feeding preferences).

It is relatively straightforward to apply these models to multiple organisms comprising food webs by linking trophic interactions, resulting in more accurate simulations and predictions for food web bioaccumulation, exposure and risk assessment.

Simple mass balance bioaccumulation models generally treat the organism as a single compartment or “box”. Physiologically-based pharmacokinetic (PBPK) models developed for medical and pharmaceutical purposes can provide more information regarding specific organs of accumulation within the body and the rates of transport and transformation within the body and excretion processes (Paterson and Mackay, 1987). More detailed models for exposure and risk assessment using PBPK models can be developed as more data become available on the processes of uptake, elimination and internal disposition of chemicals in fish and wildlife. For screening level exposure assessment objectives the simpler single “box” mass balance models are adequate and require less parameterization and data inputs. Table 2 lists a number of mass balance bioaccumulation models.

TABLE 2. Mass balance bioaccumulation models. Free downloads and descriptions of these models or links to these models are available from the website www.trentu.ca/cemc.

Model	Description	Reference
Fish	A single organism bioaccumulation model treats the steady-state uptake and loss of an organic contaminant by a fish	(Mackay, 2001)
FoodWeb	A mass balance model of contaminant flux through an aquatic food web	(Campfens and Mackay, 1997)
OMEGA	A kinetic model for food chain transfer based on chemical fugacity and biological allometry	(Hendriks et al., 2001)
FGETS	Predicts temporal bioconcentration or bioaccumulation dynamics in fish for nonionic, nonmetabolized, organic chemicals	(Barber et al., 1991)
AquaWeb	An aquatic food web bioaccumulation model	(Arnot and Gobas, 2004)
BAF-QSAR	Screening level model for bioaccumulation factors for fish in lower, middle and upper trophic levels of aquatic food webs	(Arnot and Gobas, 2003)
ACC-HUMAN	A non-steady state bioaccumulation model predicting human tissue levels from concentrations in air, soil and water	(Czub and McLachlan, 2004)
PBPK	Physiologically-based pharmacokinetic model for humans	(Cahill et al., 2003)

A general approach used in modelling chemical exposure in food webs is to assume negligible loss of chemical by metabolic biotransformation because these data are largely unavailable (Arnot and Gobas, 2006). This assumption results in the overestimation of actual chemical exposures, tissue concentrations and associated hazards and risks for chemicals that are subject to metabolic biotransformation, particularly for hydrophobic chemicals (Burkhard, 2003). Recently a QSAR model has been developed and evaluated for predicting primary biotransformation rates in fish from chemical structure (Arnot et al., 2009). The biotransformation QSAR estimates can provide valuable information to include in mass balance models to improve screening level bioaccumulation, exposure and risk assessments.

7. Exposure and Risk Assessment

In this section elements of exposure and risk assessment are reviewed and mass balance models used in regulatory programs for exposure and risk assessment are discussed. Exposure and risk assessment models combine fate and transport models with bioaccumulation models (Table 3) providing linked pathways to estimate chemical exposures. Estimated exposures can then be compared with toxicity or threshold levels for estimates of effects thus characterizing potential risks.

TABLE 3. Multimedia mass balance models that combine fate and bioaccumulation models to assess chemical exposures and risk. Free downloads and descriptions of these models or links to these models are available from the website www.trentu.ca/cemc.

Model	Description	Reference
CalTOX	A regional scale multimedia exposure model designed to assess the fate and human health impacts of contaminants	(McKone, 1993)
EUSES	EUSES brings together exposure and effect assessments and risk characterization for environmental populations and humans, including occupational and consumer scenarios at local, regional and continental scales	(Vermeire et al., 2005)
IMPACT 2002	The IMPACT 2002 model provides characterization factors for the midpoint categories: human toxicity, aquatic ecotoxicity and terrestrial ecotoxicity for life-cycle impact assessments	(Pennington et al., 2006)
RAIDAR	RAIDAR brings together chemical fate and transport, bioaccumulation, effect levels and emission rates for screening level exposure and risk assessments for humans and the environment	(Arnot and Mackay, 2008)

7.1. EXPOSURE

Chemical exposures result from a comprehensive series of events constituting multimedia exposure pathways and the rates at which organisms are exposed to chemicals in these multimedia compartments. Chemical exposures can be measured directly in monitoring programs or estimated using models. Exposure is a function of the chemical properties and the defined environment and the quantity of chemical released to the environment. Actual modeled exposure assessments require emission rate information or a method to calibrate the models to a collection of measured monitoring data. Evaluative exposure assessments using an assumed consistent "unit" emission rate for all chemicals can compare and rank chemicals based on exposure potential.

Conceptually, the source-exposure relationship includes chemical mode-of-entry to the environment (air, water, soil), fate processes (intermedia transport, degradation, advection), food web bioaccumulation processes (absorption, bioconcentration, biomagnification, biotransformation), and multimedia intake rates (inhalation and ingestion rates, dietary preferences). Metrics used to estimate exposure include daily intake rates, intake fractions and body burdens (Bennett et al., 2002; MacLeod and McKone, 2004; Cowan-Ellsberry et al., 2009). The calculations of intake rates and intake fractions are reviewed briefly below.

The daily chemical intake rates iR_i (μg/day) from exposures to multimedia sources i are calculated as

$$iR_\mathrm{i} = G_\mathrm{i}C_\mathrm{i} \tag{1}$$

where the G values are ingestion rates (g/day) and inhalation rates (m^3/day) of multimedia sources (e.g., food, water, air) and the C values are concentrations in the corresponding media i with units of (μg/g) for food and non-food items and ($\mu\mathrm{g/m}^3$) for outdoor and indoor air. The daily chemical intake rates from exposures to each media can be summed to provide the total daily intake rates iR (μg/day) as

$$iR = \Sigma iR_\mathrm{i} \tag{2}$$

The human intake fraction iF (unitless) is a hazard based metric for comparative exposure assessment calculated as (Bennett et al., 2002)

$$iF = iR/E_\mathrm{U} \tag{3}$$

where E_U is an assumed arbitrary unit emission rate (μg/day).

7.2. RISK

Risk is the probability of an adverse effect in an organism, system, or (sub) population caused under specified circumstances by exposure to an agent (WHO, 2004). Risk assessment is a process intended to calculate or estimate the risk to a given target organism, system, or (sub)population, including the identification of attendant uncertainties, following exposure to a particular agent, taking into account the inherent characteristics of the agent of concern as well as the characteristics of the specific target system (WHO, 2004). Risk can be evaluated using estimates of daily intake rates and estimates of "allowable" daily intake rates. Risk assessments can also compare an estimated or measured concentration of a substance in an organism with a concentration associated with an effect or "no effect" level.

TABLE 4. United States Environmental Protection Agency, National Library of Medicine, European Union, and Organization for Economic Cooperation and Development websites containing databases, downloadable models or links to models, model descriptions and modelling information for exposure and risk assessment.

Organization	Web site
Council for Regulatory Environmental Modeling (CREM)	www.epa.gov/crem/
National Environmental Research Laboratory (NERL)	www.epa.gov/nerl/topics/models.html
Center for Exposure Assessment and Modeling (CEAM)	www.epa.gov/ceampubl/
Atmospheric Modeling Division	www.epa.gov/asmdnerl/index.html
Support Center for Regulatory Atmospheric Modeling (SCRAM)	www.epa.gov/scram001/aqmindex.htm
National Center for Computational Toxicology (NCCT)	www.epa.gov/ncct
ECOTOX Database	cfpub.epa.gov/ecotox/
Estimation Program Interface (EPI) Suite	www.epa.gov/opptintr/exposure/pubs/episuite.htm
Hazardous Substances Data Bank	toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
Computational Toxicology	ecb.jrc.ec.europa.eu/qsar/qsar-tools/
Integrated High Production Volume Chemical Database	cs3-hq.oecd.org/scripts/hpv/
The QSAR Toolbox Project	www.oecd.org/document/23/0,3343,en_2649_34365_33957015_1_1_1_1,00.html
eChemPortal	webnet3.oecd.org/echemportal/

The focus of the present discussion is on mass balance exposure modelling; however, the assessment of risk requires information on toxicity or effect so this aspect is briefly discussed. Possible chemical effects are numerous (e.g., carcinogenic, mutagenic, reproductive, developmental, lethal); however, there are few quantitative models to predict these effects. Most effect measurements are from exposure doses or concentrations (e.g., LOAELs, median lethal dose (LD_{50})) and are often derived from the estimation of acute lethality in laboratory animals such as rodents and fish. These measured endpoints are sometimes extrapolated to other endpoints (e.g., NOAELs, Allowable Daily Intake (ADI)). A review of models to quantify acute toxicity in fish highlights the need for improvements (Moore et al., 2003). Other methods to quantify toxicity, such as critical body residues, have been proposed to reduce model uncertainty (McCarty and Mackay, 1993; Maeder et al., 2004). The OECD Toolbox (see Table 4) comprises a significant effort in recent years to integrate effects and toxicity pathway information into a user-friendly program for hazard and risk assessment.

8. Multimedia Mass Balance Models for Exposure and Risk Assessment

Examples of multimedia mass balance models used for exposure and risk assessment include CalTOX, the European Union System for the Evaluation of Substances (EUSES), IMPACT, ACC-HUMAN, and the Risk Assessment IDentification And Ranking (RAIDAR) model (McKone, 1993; Vermeire et al., 2005; Czub and McLachlan, 2004; Pennington et al., 2006; Arnot and Mackay, 2008). There are many similarities in the structure of these exposure models; however, those that include mass balance food web models (e.g., AC-HUMAN, RAIDAR) are shown to have advantages over those that include regression based bioconcentration or biotransfer models, particularly for more hydrophobic chemicals (Birak et al., 2001). As discussed previously, mass balance bio-accumulation models incorporate biomagnification (increasing concentrations at higher trophic levels) and biotransformation (decreasing concentrations at higher trophic levels) processes, thus refining exposure estimates for chemicals with similar partitioning properties.

CalTOX. CalTOX is a regional scale multimedia exposure model developed at University of California campuses and national laboratories in the United States with support from the State of California (McKone, 1993). The model is designed to assess the fate and human health impacts of contaminants and comprises of two principal components. The first calculates multimedia transport and transformation in air, water, soil and sediment and the second translates these environmental concentrations into estimates of human exposure and potential dose. Potential doses are derived as products of chemical concentrations in contact media and contact factors for each media. Concentrations in fish are estimated using a BCF regression model and concentrations in meat, milk and eggs are estimated using the BTF model derived by Travis and Arms (Travis and Arms, 1988). The model includes inputs for cancer and non-cancer endpoints for hazard and risk calculations.

EUSES. EU Member States, the European Commission and the European Chemicals Industry have developed the European Union System for the Evaluation of Substances (EUSES) (Vermeire et al., 2005). EUSES brings together exposure and effect assessments and risk characterization for environmental populations and humans, including occupational and consumer scenarios. The main modules include inputs, emissions, distribution (fate and transport), exposure, effects, risk characterization, and outputs. Distribution follows the Mackay concept and includes three nested scales (Den Hollander et al., 2004). Chemical concentrations in fish are estimated using BCF-QSAR models (Veith et al., 1979; Connell and Hawker, 1988). Concentrations in human dietary sources are estimated from QSARs, namely BCFs and BTFs (Travis and Arms, 1988; Trapp and Matthies, 1995). The daily dose for humans is calculated by means of the concentrations in these media and the daily intake values. Effect endpoints included are predicted no-effect concentrations (PNECs), median lethal concentration (LC_{50}), and median effect concentration (EC_{50}) for environmental receptors and no observed adverse effect levels (NOAELs) from rat data for humans.

The QSARs and empirical regressions used in CalTOX and EUSES to simulate food web bioaccumulation and estimate exposures do not account for chemical-specific processes that can lead to increased (biomagnification) or decreased (biotransformation) chemical concentrations in various organisms. This treatment of food webs has been cited as a major need for improvement in current multimedia models used for ecological and human health risk assessment (Rikken and Lijzen, 2004; Birak et al., 2001).

RAIDAR. The Risk Assessment, IDentification, And Ranking (RAIDAR) model brings together chemical fate and exposure and effect in an evaluative mass balance modelling framework to screen potential ecological and human health risks from chemicals released to the environment (Arnot et al., 2006). RAIDAR includes mechanistic mass balance food web bioaccumulation models to account for chemical specific biomagnification and biotransformation processes. The food webs are representative of aquatic and terrestrial species such as vegetation, invertebrates, fish, wildlife, agricultural species and humans. To address the uncertainty associated with determining accurate actual chemical emission rates, RAIDAR first uses a hypothetical unit emission rate to identify the most sensitive receptor based on a consistent effect endpoint from which a critical emission rate is calculated. The critical emission rate is then compared to actual emission rate estimates providing a screening level metric of risk, the risk assessment factor (RAF). The RAFs for a list of chemicals can readily be compared and ranked to prioritize more comprehensive evaluation. Environmental quality guidelines or critical body residues can be used for the screening level risk assessments.

RAIDAR also calculates exposure assessment factors (EAFs) and hazard assessment factors (HAFs) to rank chemicals based on exposure and hazard assessment objectives (Arnot and Mackay, 2008). The EAF combines persistence and bioaccumulation properties of the chemical into a single value for exposure assessment comparisons. The HAF combines persistence, bioaccumulation and toxicity properties into a single metric for transparent chemical screening evaluations.

9. Conclusion

The limited measured and monitoring data currently available necessitates the use of QSARs and mass balance models to prioritize chemicals for more comprehensive evaluations. Exposure and risk assessment modelling is relatively inexpensive and easy compared to extensive human and environmental monitoring programs. Mass balance fate and transport, food web bioaccumulation, and exposure models have been evaluated to a limited extent when monitoring data are available (Matthies et al., 2004; Kelly and Gobas, 2003; Arnot and Gobas, 2004; Armitage et al., 2007; Cowan-Ellsberry et al., 2009). Clearly there is a need to integrate modelling and monitoring programs to further refine models, improve scientific knowledge for chemical exposures to humans and ecological receptors, and add credibility to regulatory programs. There is a need to improve mass balance models, particularly for certain types of chemicals such as ionizing substances and perfluorinated surfactants, and for regions with extreme climates such as tropical and arctic regions. Without a comprehensive program models used in regulatory programs may underestimate exposure and risk resulting in adverse effects to humans or ecosystems. Conversely, if exposure and risk are overestimated this will result in unnecessary costs and restrictions to industry and reduced societal benefits.

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EXPOSURE AND RISK ASSESSMENT MODELING TO SCREEN AND PRIORITIZE COMMERCIAL CHEMICAL INVENTORIES

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Abstract. National and international regulatory programs seek to evaluate the exposures, hazards and risks chemicals may pose to humans and the environment. There are many chemicals of commerce requiring assessment and few measured data available thus requiring the application of models for screening level assessments. Current methods for priority setting use "bright line" cut-off criteria in multiple categories such as persistence (P), bioaccumulation (B), toxicity (T), and quantity (Q). The present study illustrates the application of a novel holistic mass balance modelling method to screen and prioritize chemical inventories for exposures and risks to ecological receptors and humans. The RAIDAR model is used to combine P and B information into an exposure assessment factor (EAF), and P, B, T and Q into a risk assessment factor (RAF) providing single values for transparent comparisons and rankings based on exposure and risk objectives. The present study also includes estimates of biotransformation in food webs in the screening level calculations. The method is illustrated as a case study using 30 organic chemicals selected from the Canadian Domestic Substances List. The priority setting results of the cut-off based categorization are largely inconsistent with the proposed holistic mass balance modelling method. Current "bright line" category based methods are shown to be largely ineffective at prioritizing those chemicals that pose the greatest risks to humans and the environment. It is suggested that in order to minimize potential errors in preliminary stages of chemical assessments, complementary holistic methods for priority setting such as those proposed in the present study should be considered.

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Keywords: mass balance models, fate and transport, bioaccumulation, exposure assessment, risk assessment

1. Introduction

Chemical assessment methods and criteria developed over the past 40 years are now being applied broadly in a regulatory context (Government of Canada, 1999; UNEP, 2001; Lahl and Hawxwell, 2006). Globally, it is estimated that as many as 100,000 existing chemicals and 1,000–2,000 new substances developed annually require evaluation for their potential adverse effects on the environment and human health (Muir and Howard, 2006). In contrast to the many chemicals requiring assessment, there are relatively few measured data available for concentrations in the environment and for chemical properties such as partitioning, reactivity and toxicity (Arnot and Gobas, 2006; Environment Canada, 2006). This necessitates the use of Quantitative Structure–Activity Relationships (QSARs) and mass balance models, at least for preliminary screening and priority setting evaluations.

There is a need to focus immediate effort on chemicals of greatest concern; however, setting such priorities is challenging. While reducing the risk of adverse effects is the fundamental objective, the general evaluation strategy used in current methods is to first categorize chemicals for hazard properties and then subject those that are considered to be hazardous for more comprehensive risk assessment. Hazard-based categorizations compare intrinsic chemical properties against selected criteria in specified and separate categories such as persistence (P), bioaccumulation (B), and toxicity (T). Numeric "cut-off" criteria are used for each category such that a chemical receives a binary assignment as satisfying or not satisfying a selected cut-off criterion (e.g., "B" or "not B"). Muir and Howard (2006) provide a summary of the regulatory criteria used in different jurisdictions. Using three hazard categories a chemical can fall into one of eight classes (e.g., "P, B, T", or "P, not B, T" or "not P, not B, not T"). A recent study highlights flaws in the current methodology and proposes that a novel holistic method may be better for priority setting or at least complementary to existing assessment programs (Arnot and Mackay, 2008).

The present study illustrates the proposed holistic method using the Risk Assessment IDentification And Ranking (RAIDAR) model (Arnot et al., 2006; Arnot and Mackay, 2008). Fundamentally, risk is a function of the rate, or quantity (Q), of chemical released to the environment; fate, transport and persistence (P) in the physical environment (air, water, soil, sediment); bioaccumulation (B) in plants and animals; and toxicity (T) (Arnot and Mackay, 2008). Elements of P and B determine the potential for chemical exposure while QPB determine actual exposures. The RAIDAR mass balance model combines P and B information into an exposure assessment factor (EAF), and P, B, T and estimated emissions quantity (Q) into a risk assessment factor (RAF) thus providing single values for transparent chemical comparisons and rankings based on exposure and/or risk objectives. The present study also includes estimates of biotransformation in food webs using a QSAR model that has recently been developed and evaluated (Arnot et al., 2009). The holistic method is illustrated as a case study for exposure and risk priority setting using 30 organic chemicals selected from the Canadian Domestic Substances List (DSL). The RAIDAR model results are compared with current "bright line" hazard category priority setting methods used in Canada (Government of Canada, 1999) and in other regulatory programs such as the REACH program in Europe (Lahl and Hawxwell, 2006).

2. Model Description

Table 1 summarizes physical and biological characteristics of the RAIDAR Ver.2.0 model. Details are provided elsewhere (Arnot and Mackay, 2008). Briefly, RAIDAR is a screening level evaluative model that combines information on chemical partitioning, degradation, environmental fate and transport, food web bioaccumulation, exposure, effect endpoint and emission rate in a coherent mass balance framework. The default environment includes a regional landscape with an area of 100,000 km^2 (~90% land, ~10% water with underlying sediment). RAIDAR includes a variety of representative plant, invertebrate and vertebrate species including fish, wildlife, agricultural crops and livestock, and humans. The mechanistic mass balance food web bioaccumulation models calculate concentrations in the representative species from exposures to chemical in the ambient environment and in the diet. Primary producers and invertebrates bioconcentrate chemical from their ambient environment of air, water, soil, or sediment while all other species bioaccumulate chemical from their ambient environment and from their diet. The mass balance modelling approach includes major routes of chemical uptake and elimination. Chemical-specific biomagnification and biotransformation processes, which can result in orders of magnitude difference in bioaccumulation estimates for chemicals with the same partitioning properties, are thus accounted.

Only farfield exposures are currently considered for humans. The model does not include occupational or industrial exposures or indoor air and consumer product uses (e.g., personal care or household products). It is assumed that there are no losses or additions of chemical to food as a result of processing (e.g., animal husbandry) and preparation (e.g., cooking, washing).

TABLE 1. Physical compartments and representative biological species in the RAIDAR Ver. 2.0 evaluative environment.

Bulk physical compartments (sub phases)
Air (gaseous and aerosol)
Water (water and suspended solids)
Soil (gaseous, water and solids)
Sediment (water and solids)
Aquatic organisms (representation)
Plankton (e.g., phytoplankton)
Benthic invertebrate (e.g., bivalve)
Lower trophic level fish (e.g., smelt)
Upper trophic level fish (e.g., salmonid)
Mammal (e.g., seal, beluga whale)
Terrestrial organisms (representation)
Foliage vegetation – above ground (e.g., fruits, grasses)
Root vegetation – below ground (e.g., carrots, roots)
Terrestrial invertebrate (e.g., worm)
Terrestrial herbivore (e.g., deer)
Terrestrial carnivore (e.g., wolf)
Avian omnivore (e.g., robin)
Avian scavenger (e.g., eagle)
Agricultural – swine (e.g., pigs, pork)
Agricultural – cattle (e.g., beef and dairy)
Agricultural – poultry (e.g., broilers and hens)
Human (e.g., adult male)

3. RAIDAR Exposure and Risk Calculations

Chemical exposures to humans and ecological receptors result from a comprehensive series of events constituting multimedia exposure pathways and the rates at which organisms are exposed to chemical concentrations in these multimedia compartments. Conceptually, the source–exposure relationship includes the emission of chemical to the environment, chemical mode-of-entry to the environment (air, water, soil), fate processes (intermedia transport, degradation, advection), food web bioaccumulation processes (biomagnification, biotransformation), and multimedia intake rates (inhalation and ingestion rates, dietary preferences).

Risk is the probability of an adverse effect in an organism, system, or (sub)population caused under specified circumstances by exposure to an agent (WHO, 2004). Risk assessment is a process intended to calculate or estimate the risk to a given target organism, system, or (sub)population, including the identification of attendant uncertainties, following exposure to a particular agent, taking into account the inherent characteristics of the agent of concern as well as the characteristics of the specific target system (WHO, 2004).

The RAIDAR exposure and risk calculations are briefly summarized here, while details are provided elsewhere (Arnot and Mackay, 2008). The calculation of the RAF is comprised of four steps. First, the model calculates chemical fate and transport in the environment using mass balance equations for an arbitrary unit emission rate (E_U; e.g., 1 mol h^{-1}). The user of the model can decide whether to use Level II or Level III fate calculations. If Level III calculations are desirable the user must select a mode-of-entry for the chemical to the environment, i.e., emissions to air, or water, or soil or a combination of the three. The fate calculations include environmental persistence and determine the steady state concentrations in environmental media (air, water, soil, and sediment). Second, the model calculates the transfer of chemical from the physical compartments of the environment to the representative biological species. The combined fate and bioaccumulation calculations thus provide unit emission based concentrations in all of the representative organisms C_U (mol m^{-3}). Third, calculated C_U values are compared to whole body concentrations for a threshold (toxic) effect endpoint C_T (mol m^{-3}). The organism with the highest C_U/C_T ratio is identified and this determines the critical emission rate E_C (mol h^{-1}) (Arnot et al., 2006). The critical emission rate is the rate corresponding to an exposure concentration, i.e., C_U, which exceeds the selected concentration threshold, i.e., C_T. The final stage is to include the actual emission rate E_A (mol h^{-1}), which is an estimated rate of release (Q). The ratio E_A/E_C provides a screening level metric for risk.

Thus the RAIDAR RAF (dimensionless) is a combined function of P, B, T and Q for each chemical and is calculated as (Arnot and Mackay, 2008)

$$\text{RAF} = (C_U/C_T)\,(E_A/E_U) = E_A/E_C \tag{1}$$

RAFs among chemicals can then be compared and ranked. Chemicals with higher risk potential have higher RAFs.

The model also calculates an exposure assessment factor (EAF; h m^{-3}). In Equation 1 this is the ratio C_U/E_U. The EAF ratio does not include an estimate for actual emissions or a toxicity threshold value. The combined fate and bioaccumulation models calculate the EAF for each chemical and for each representative species in the model. Thus, the EAF combines P and B information and provides for transparent assessments of chemical exposure potential. The highest EAFs identify the species that are most vulnerable to contamination. For each chemical a maximum EAF value can be selected for chemical comparisons and rankings. Of course, the product of the EAF and the unit emission rate E_U is the whole body unit concentration C_U as calculated for all representative species. The model can be used to calculate estimates of expected concentrations if actual emission rates are known.

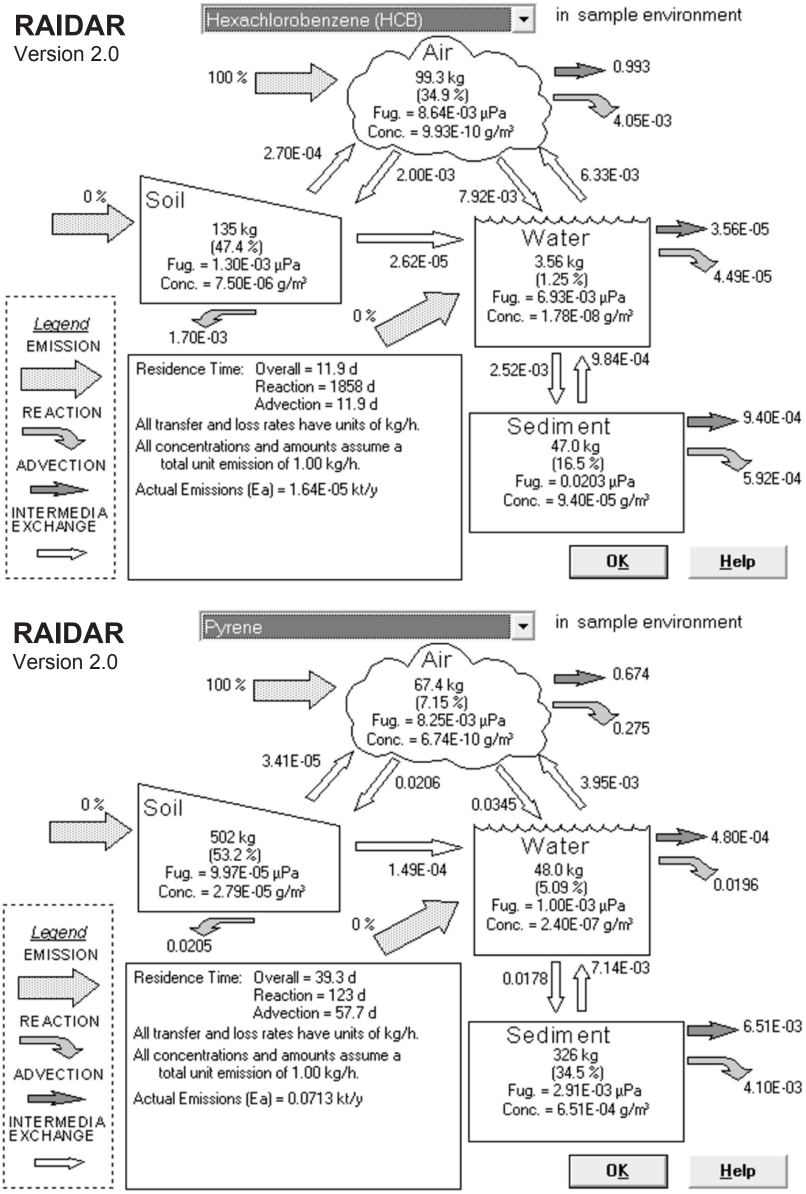
The RAIDAR model also calculates a hazard assessment factor (HAF; dimensionless) for each chemical. The HAF brings together information on P, B and T as a single metric allowing for transparent comparisons and ranking of chemicals based on combined hazard categorization properties (Arnot and Mackay, 2008). In Equation 1 this is the ratio C_U/C_T. This ratio is calculated for each representative organism and the largest ratio identifies those species subject to greatest combined hazard. The HAF is not detailed or calculated in the results of the present study; however, details on this metric and how it relates to the EAF and RAF are available elsewhere (Arnot and Mackay, 2008).

4. Model Application

Two case studies are provided for comparative exposure and risk assessment evaluations using the RAIDAR Ver.2.0 model (Arnot and Mackay, 2008). The first is a detailed illustration of the calculations and the model fate, bioaccumulation, EAF and RAF results for two chemicals. The second is a larger scale application to 30 chemicals listed on the Canadian DSL. Advective loss processes are "shut off" in the RAIDAR model for these assessments because advection from one region to another region can underestimate the actual exposure and risk potential of a chemical (Webster et al., 1998). An exception is for the fate distribution diagrams and associated discussions (see Figure 1 below) for which default advective flow residence times were used to highlight the importance of advective loss processes for certain chemicals and the need to consider this assumption in screening level assessment objectives.

4.1. CASE STUDY #1

Table 2 lists the input data required for hexachlorobenzene and pyrene RAIDAR EAF and RAF calculations. The selected threshold effect endpoint is acute lethality. The threshold endpoint must be consistent for all species and all chemicals for comparative hazard and risk evaluations (Arnot et al., 2006). Other effect endpoints should eventually be considered; however, data are limited for the large numbers of chemicals requiring assessment. For the Level III RAIDAR fate calculations it is assumed that 100% of the emissions are to air, which is consistent with chemical emissions data for hexachlorobenzene and pyrene in Canada (Environment Canada, 2008). An arbitrary unit emission rate E_U of 1 kg h^{-1} is chosen for both chemicals.



Residence Time: Overall = 11.9 d
Reaction = 1858 d
Advection = 11.9 d

All transfer and loss rates have units of kg/h.

All concentrations and amounts assume a total unit emission of 1.00 kg/h.

Actual Emissions (Ea) = 1.64E-05 kt/y

Residence Time: Overall = 39.3 d
Reaction = 123 d
Advection = 57.7 d

All transfer and loss rates have units of kg/h.

All concentrations and amounts assume a total unit emission of 1.00 kg/h.

Actual Emissions (Ea) = 0.0713 kt/y

Figure 1. RAIDAR v.2.0 Level III chemical fate diagrams for hexachlorobenzene (*upper*) and pyrene (*lower*) based on an assumed unit emission rate of 1 kg h^{-1} to air.

Figure 1 shows the fate distribution diagrams for the two chemicals in the RAIDAR evaluative environment. Hexachlorobenzene is distributed primarily to soils (47.4%) and air (34.9%), whereas pyrene is distributed primarily to soils (53.2%) and sediment (34.5%). At steady state approximately 99% and 67% of the losses from the regional environment for hexachlorobenzene and pyrene, respectively, are by advection in air. The advection residence time (τ_A) is shorter for hexachlorobenzene than it is for pyrene. The τ_A for hexachlorobenzene is 11.9 days and for pyrene τ_A is 57.7 days. The reaction residence time (τ_R) is a better indicator for actual chemical persistence because this calculation does not include advective losses, i.e., moving from one region to another (Webster et al., 1998). The reaction residence time approximates the time required for two-thirds of the parent chemical present in the system to be transformed by reactive (degradation) processes. The τ_R for hexachlorobenzene is 1,858 days and for pyrene τ_R is 123 days. The overall residence time (τ_O) is calculated as $1/\tau_O = 1/\tau_A + 1/\tau_R$. Therefore, although the τ_O for hexachlorobenzene is about four times shorter than pyrene, hexachlorobenzene is about 15 times more persistent. As mentioned previously, this highlights the need to address the implications of including, or not including, advective loss processes for comparative assessments of persistence, exposure and risk.

Figure 2a shows the calculated unit concentrations (C_U; mol m^{-3}) for both chemicals for selected representative species. Hexachlorobenzene has higher unit concentrations in all species. The bioaccumulation factor (calculated as the concentration ratio: Cfish/Cwater) for hexachlorobenzene in the upper trophic level fish is 350,000 (L kg^{-1}) and for pyrene it is 760 (L kg^{-1}). Thus, hexachlorobenzene is about 460 times more bioaccumulative in fish than pyrene. The maximum EAF, i.e., C_U/E_U (h m^{-3}) for hexachlorobenzene is 2.2×10^{-2} as determined by exposures to marine mammals. The maximum EAF for pyrene is 1.9×10^{-5} as determined by exposures to benthic invertebrates. Thus, the maximum exposure potential (combining P and B information) is about 1,200 times greater for hexachlorobenzene.

To calculate the RAFs the next step is to include toxicity (C_T; mol m^{-3}) and actual emissions (E_A; mol h^{-1}) information from Table 1. For hexachlorobenzene, the ratio C_U/E_U (EAF) is 2.2×10^{-2} (h m^{-3}) and the ratio E_A/C_T is 0.00132 (m^3 h^{-1}). Thus, the RAF is 2.9×10^{-5}, the product of these two ratios (Equation 1). For pyrene, the ratio C_U/E_U (EAF) is 1.9×10^{-5} (h m^{-3}) and the ratio E_A/C_T is 8 (m^3 h^{-1}), thus the RAF is 1.5×10^{-4}. These results suggests that based on current actual emission rate estimates in Canada pyrene poses a greater potential risk than hexachlorobenzene. This is contradictory to the observed greater exposure potential for hexachlorobenzene. The difference between actual exposure and risk is the result of greater emissions associated with pyrene, since the selected toxicity threshold values are equivalent.

Inspection of Equation 1 also shows that risk calculations, i.e., RAFs, are proportional to toxicity threshold values and actual emission rate estimates. For example, if the estimated actual emission rate increases by a factor of 10 then the estimated risk will increase by a factor of 10. The sensitivity in the calculations highlights the need for reliable values for E_A and C_T for reliable estimates of risk.

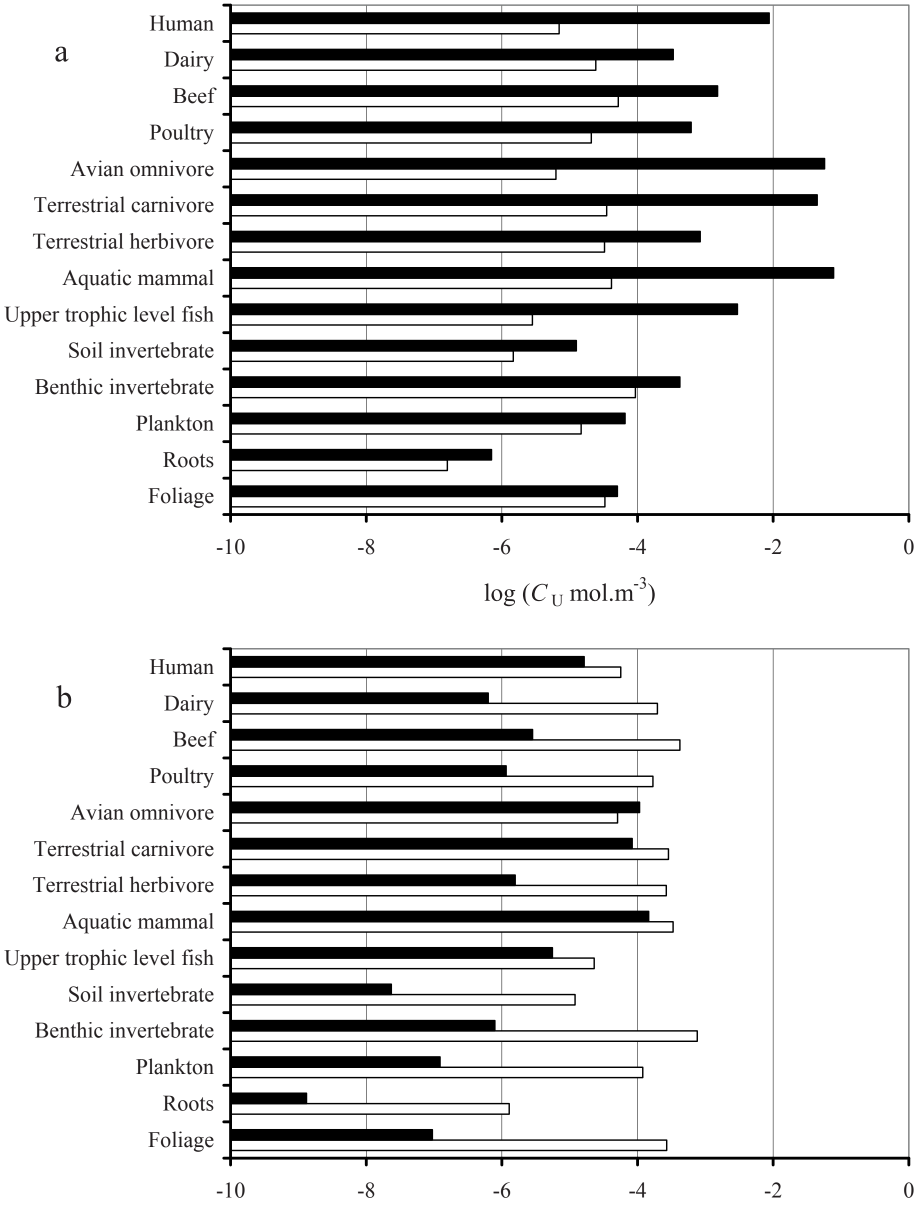


Figure 2. Estimated concentrations in selected representative species for hexachlorobenzene and pyrene. (**a**) concentrations based on a consistent unit emission rate for both chemicals (1 kg h^{-1}); (**b**) based on estimated actual emission rates (see text).

The linearity of the model calculations can also be exploited for the exposure estimates. Figure 2b shows the estimated concentrations (C_A; mol m^{-3}) for both chemicals for selected representative species based on estimates of actual emission rates E_A. The C_A concentration estimates are derived by scaling the estimated unit concentrations C_U by the ratio E_A/E_U. The concentrations in pyrene are higher than the concentration for hexachlorobenzene because the actual emissions are estimated to be approximately 4,350 times greater for pyrene. It must be recognized that in Canada hexachlorobenzene is a regulated chemical and emissions to the environment have been restricted for several years. Hexachlorobenzene is a persistent organic pollutant and actual biological concentrations from monitoring data are generally expected to still be higher for hexachlorobenzene than for pyrene because of this fact. A better way to evaluate the model with monitoring data for hexachlorobenzene and other persistent organic pollutants is to calibrate the unit emission rate to obtain agreement between estimated and observed concentrations in various multimedia compartments (McKone et al., 2007).

TABLE 2. Input parameters for hexachlorobenzene and pyrene for RAIDAR exposure and risk assessment modelling. Chemical property values selected from (Mackay et al., 2006) and biotransformation half-lives in fish were selected from (Arnot et al., 2009). Biotransformation half-lives (HL_N) in biota are listed normalized to 1 kg body size and scaled to mass (M_i; kg) specific values (HL_i) for different species in the model as $HL_i = HL_N \times (M_i/1)^{-0.25}$. HL values for higher order vertebrates are assumed ~1/3 of fish HL values. K_{OW}: octanol-water partition coefficient; C_T: whole body wet weight threshold effect concentration (values selected from (Environment Canada, 2006)); E_A: estimated actual emission rate (values selected from (Environment Canada, 2008)).

Parameter	Hexachlorobenzene	Pyrene
CAS Registration No.	118-74-1	129-00-0
Molar mass, g mol^{-1}	284.78	202.25
Vapor pressure, Pa	0.0023	0.0006
Water solubility, g m^{-3}	0.005	0.132
log K_{OW}, unitless	5.5	5.18
Half-lives, h		
Air	17,000	170
Water	55,000	1,700
Soil	55,000	17,000
Sediment	55,000	55,000
Fish	19,000	150
Birds/Mammals	6,300	50
C_T, mol m^{-3}	5	5
E_A, mol h^{-1}	0.0066	40

4.2. CASE STUDY #2

Table 3 lists the names and CAS registration numbers for 30 chemicals selected from the Canadian DSL to illustrate the comparative exposure and risk estimates. Physical-chemical properties and environmental half-lives were obtained from the EPI Suite QSAR model and database (U.S. EPA, 2007). Biotransformation estimates were obtained from the fish biotransformation rate QSAR (Arnot et al., 2009). The toxicity threshold values and estimates for actual emission rates were obtained from the Canadian DSL database (Environment Canada, 2006) using methods described earlier (Arnot and Mackay, 2008). An arbitrary unit emission rate of 1 kg h^{-1} was used. For this case study, Level II RAIDAR fate calculations were chosen; therefore, information for mode-of-entry to the environment was not required. Other than the biotransformation estimates, the same basic data used in the DSL categorization was used in the RAIDAR mass balance modelling methods.

The DSL chemicals have been categorized according to regulations in the Canadian Environmental Protection Act as meeting screening level hazard based "bright line" criteria or not meeting screening level hazard based "bright line" criteria (Government of Canada, 1999). The DSL chemicals that meet the criteria are considered "in" and may be subject to further evaluations such as risk assessments. The DSL chemicals that do not meet the criteria are considered "out" and are not subject to further evaluations. Chemical ID# 1 in Tables 3 and 4 is hexachlorobenzene and is also a listed Stockholm Convention Persistent Organic Pollutant (POP). Hexachlorobenzene thus provides a benchmark for the exposure potential calculations and chemical comparisons.

Table 4 lists, and Figure 3 illustrates, the RAIDAR calculated EAFs and RAFs for the 30 chemicals. The left side of the graph (Chemical ID# 1–15) shows categorized "DSL in" chemicals and the right side of the graph (Chemical ID# 16–30) shows categorized "DSL out" chemicals. The EAFs are "maximum" values for each chemical as identified from the species with the highest exposure potential based on a consistent assumed unit emission rate for all chemicals.

The EAFs range approximately 9 orders of magnitude. The exposure potential is greatest for hexachlorobenzene (log EAF = –2.2). Other chemicals that are categorized "in" with high exposure potential are heptabromodiphenyl ether (a brominated flame retardant), 1,3,5-tribromobenzene, and pyrene (a polycyclic aromatic hydrocarbon). Some chemicals categorized "out" using current screening methods also have comparable exposure potential including decabromodiphenyl ether (a brominated flame retardant) and phenanthrene (a polycyclic aromatic hydrocarbon). Figure 3 shows that a number of chemicals categorized "out" have exposure estimates greater than chemicals categorized "in".

TABLE 3. List of chemicals used in case study #2.

ID#	CAS Reg No	Category	Chemical name
1	118-74-1	POP	Hexachlorobenzene
2	523-31-9	In	Dibenzyl phthalate
3	86-74-8	In	9H-Carbazole
4	95-51-2	In	Benzenamine, 2-chloro-
5	68928-80-3	In	Heptabromodiphenyl ether
6	1579-40-4	In	Benzene, 1,1 -oxybis[4-methyl-
7	626-39-1	In	Benzene, 1,3,5-tribromo-
8	28178-42-9	In	2,6-Diisopropylphenyl isocyanate
9	108-90-7	In	Benzene, chloro-
10	592-82-5	In	Butane, 1-isothiocyanato-
11	2921-88-2	In	Chlorpyrifos
12	6221-92-7	In	Cyclododecanol, acetate
13	106-93-4	In	Ethane, 1,2-dibromo-
14	556-61-6	In	Methane, isothiocyanato-
15	129-00-0	In	Pyrene
16	123-31-9	Out	1,4-Benzenediol
17	71-36-3	Out	1-Butanol
18	107-05-1	Out	1-Propene, 3-chloro-
19	591-78-6	Out	2-Hexanone
20	107-87-9	Out	2-Pentanone
21	1163-19-5	Out	Decabromodiphenyl ether
22	271-89-6	Out	Benzofuran
23	107-06-2	Out	Ethane, 1,2-dichloro-
24	50-00-0	Out	Formaldehyde
25	109-87-5	Out	Methane, dimethoxy-
26	122-60-1	Out	Oxirane, (phenoxymethyl)-
27	85-01-8	Out	Phenanthrene
28	96-18-4	Out	Propane, 1,2,3-trichloro-
29	79-06-1	Out	2-Propenamide
30	62-56-6	Out	Thiourea

TABLE 4. Logarithms for the maximum EAF values and RAF values for the case study #2 chemicals.

ID#	Cat.	Chemical name	Log EAF	Log RAF
1	POP	Hexachlorobenzene	−2.2	−5.1
2	In	Dibenzyl phthalate	−6.8	−7.1
3	In	9H-Carbazole	−6.6	−7.9
4	In	Benzenamine, 2-chloro-	−8.1	−6.9
5	In	Heptabromodiphenyl ether	−4.6	−2.6
6	In	Benzene, 1,1 -oxybis[4-methyl-	−6.3	−7.7
7	In	Benzene, 1,3,5-tribromo-	−4.8	−6.4
8	In	2,6-Diisopropylphenyl isocyanate	−7.9	−9.3
9	In	Benzene, chloro-	−9.1	−5.8
10	In	Butane, 1-isothiocyanato-	−8.8	−8.4
11	In	Chlorpyrifos	−6.0	−7.6
12	In	Cyclododecanol, acetate	−7.3	−8.8
13	In	Ethane, 1,2-dibromo-	−8.4	−1.7
14	In	Methane, isothiocyanato-	−8.6	−5.9
15	In	Pyrene	−5.1	−4.2
16	Out	1,4-Benzenediol	−8.8	−1.9
17	Out	1-Butanol	−9.3	−6.3
18	Out	1-Propene, 3-chloro-	−11.0	−7.7
19	Out	2-Hexanone	−9.4	−8.5
20	Out	2-Pentanone	−9.6	−6.7
21	Out	Decabromodiphenyl ether	−4.9	−5.0
22	Out	Benzofuran	−9.1	−8.3
23	Out	Ethane, 1,2-dichloro-	−8.6	−5.8
24	Out	Formaldehyde	−9.9	−3.8
25	Out	Methane, dimethoxy-	−10.0	−7.0
26	Out	Oxirane, (phenoxymethyl)-	−8.3	−9.6
27	Out	Phenanthrene	−6.1	−6.4
28	Out	Propane, 1,2,3-trichloro-	−7.9	−8.0
29	Out	2-Propenamide	−8.9	−2.9
30	Out	Thiourea	−8.9	−5.9

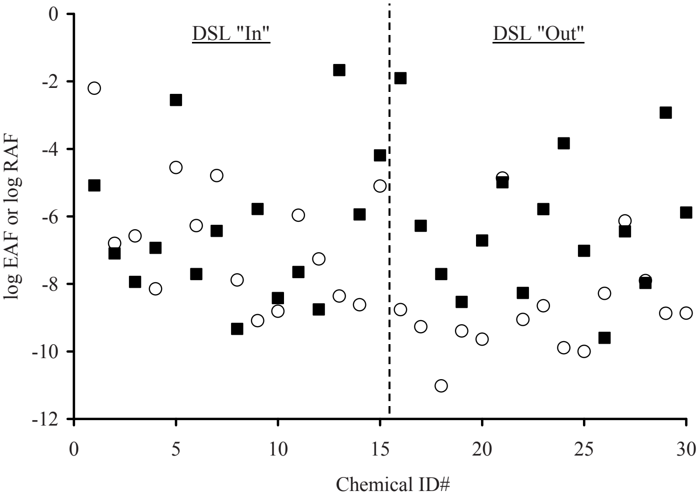


Figure 3. A comparison of maximum EAF and RAF model estimates for 30 case study DSL chemicals. Chemical ID#s refer to chemical listings in Tables 3 and 4. closed boxes: RAF; open circles: EAF.

The RAIDAR RAFs for the 30 DSL chemicals range approximately 8 orders of magnitude. The risk potential is greatest for 1,2-dibromoethane. Other chemicals that are categorized "in" with high risk potential are heptabromodiphenyl ether and pyrene. Certain chemicals categorized "out" using current screening methods also have comparable risk potential as those categorized "in" including 1,4-benzenediol, formaldehyde, and 2-propenamide. Clearly, chemicals that are not considered for further evaluation have equivalent or greater risk potential than chemicals that may be further assessed. Conversely, many chemicals that may be assessed for risk ("in") have lower risk potential than chemicals categorized "out" using existing methods and criteria. The median log RAF (–6.4) from the "categorized out" group of chemicals is higher than the median log RAF (–6.9) for the "categorized in" group. These data suggest that current multiple bright line hazard criteria methods do not effectively discriminate "high risk" chemicals from "low risk" chemicals. This is a concern provided the need to assess these chemicals in a timely manner (they have been used in commerce for decades), and the limited resources (money, people power) available to conduct these assessments. For example, relatively "low risk" chemicals that are categorized "in" using existing methods in Canada or Europe may be subject to substantial evaluations including needless animal testing.

There are large differences between RAF (risk) and EAF (exposure potential) estimates for the same chemical. For example, the RAF for 1,4-benezenediol is 7 orders of magnitude higher than the maximum EAF for the chemical. This issue was also highlighted in the case study #1. Chemicals ranked for exposure potential will rank very differently for risk potential because of the influence of actual emission rates and toxicity. This reiterates the need to obtain reliable estimates for toxicity and emissions for effective chemical evaluations and management.

4.3. MERITS AND LIMITATIONS

The general purpose of the RAIDAR model is to screen organic chemicals for potential exposures, hazards and risks to humans and the environment using available data. After screening chemical lists and inventories those chemicals that rank highest can be prioritized for critical inspection of the results and the available data used to obtain the results. Further, those chemicals that remain of high concern can then be subject to more comprehensive evaluations using more sophisticated models (e.g., site-specific), improved data (e.g., better estimates for actual emission rates and toxicity) and preferably using targeted monitoring data from the environment and humans. An obvious strategy would be to strategically measure chemical concentrations in the environment by directing monitoring studies based on the model results. For example, sample and measure the physical compartments (e.g., sediment) or trophic levels (e.g., benthic invertebrates) that the model predicts to have the highest concentrations.

Ostensibly, current regulatory assessment objectives are to identify chemicals with the greatest potential for exposure and/or risk. The holistic modelling approach described here provides a scientifically defensible approach to combine available data for priority setting based on these objectives and avoid the pitfalls of multiple "bright-line" cut-off criteria. A complete discussion on the pitfalls of using multiple "bright-line" cut-off criteria for priority setting is beyond the scope of the present study; however, some key findings are reiterated (Arnot and Mackay, 2008). The use of multiple categories requires subjective interpretation of the various category scores, e.g., "P and B, but not T". If chemical "X" exceeds P and B criteria but not T and chemical "Y" exceeds T and B criteria but not P, which chemical is a higher priority for assessment? The holistic approach provides single values for each chemical for direct comparisons and rankings. What if a substance is just below or above a bright-line cut off value? Furthermore, there is substantial uncertainty and variability in the measured and estimated values being used to compare against the bright line criteria at preliminary stages using existing methods (Arnot and Gobas, 2006); however, this uncertainty is not considered. Sensitivity and uncertainty analyses can be included in the mass balance model calculations for exposure and risk, thus including uncertainty in the risk assessment and guiding needs for model and data input improvements (MacLeod et al., 2002). The errors associated with directly using exposure based aquatic toxicity data for toxic potency comparisons (e.g., median lethal concentration) are well recognized (McCarty and Mackay, 1993; Maeder et al., 2004). The holistic method uses critical body residues as a means to alleviate these errors (Arnot and Mackay, 2008).

A pragmatic approach after ranking chemicals with the holistic mass balance modelling methods would be to start with the highest ranked chemicals and critically inspect the results, the input values and the underlying assumptions. In particular, the reliability of the emission and toxicity estimates need to be considered. For example, inspection of the toxicity value selected from the Environment Canada categorization in the present case study for 1,2-dibromoethane suggests that the value for this chemical is not consistent with other endpoints (acute lethality). Further, the modelling results directly relate to the underlying assumptions of the model and are not readily applicable to all chemicals. At present, the RAIDAR model only accounts for "farfield" exposures to humans; therefore, consideration is required for potential personal uses and indoor exposures for humans and for occupational exposures. If large quantities of a chemical are released at a particular site then site-specific models and assessments should be conducted for that chemical. The QSARs and models need to be improved for certain classes of chemicals (e.g., perfluorinated organics and other ionizing chemicals, certain dyes and pigments). Not withstanding the present limitations of applying models to "model difficult" substances, the issues surrounding "model difficult" substances complicates current assessment methods as well since they also rely on similar models.

5. Conclusion

The priority setting results using existing methods are not consistent with those of the proposed holistic method. In particular, many chemicals screened "out" using the current multiple bright line cut-off criteria methods are shown to pose greater potential risk than chemicals screened "in". A suggested strategy for chemical assessment programs is to combine model application and hypothesis generation with strategic monitoring programs to test, evaluate and thus improve the models in a progressive scientific manner while addressing regulatory objectives using the best available knowledge. Recognizing the requirement for using QSARs and mass balance models in chemical assessment programs, this defensible approach to method refinement would add further credibility to assessment decisions. Undoubtedly, the science of chemical exposure and risk assessments is an ongoing evolution; therefore, current chemical regulatory and management programs need to be adaptive. Chemical assessment methods developed in previous decades have recognized limitations. The present study highlights that in order to minimize potential errors in preliminary stages of chemical assessments, complementary holistic methods for priority setting should be considered.

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METHODOLOGY FOR EXPOSURE AND RISK ASSESSMENT IN COMPLEX ENVIRONMENTAL POLLUTION SITUATIONS

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Abstract. Frequently environmental pollution results from different hazardous substances released in the environment, meaning that contaminated sites may have many different chemical sources and transport pathways. Problems concerning environmental pollution affect mainly physical, chemical and biological properties of air, water and soil. The relationships between the sources, exposure and effects of contaminants to human and ecological receptors are complex and many times are specific to a particular site, to certain environmental conditions and to a particular receptor. Often the methodology for exposure and risk assessment to environmental pollution is translated into sets of assessment questions. These questions are used to meet the needs of assessment, particular important in focusing the assessment during the problem formulation. Risk assessments vary widely in scope and application. Some look at single risks in a range of exposure scenarios, others are site-specific and look at the range of risks posed by a facility. In general, risk assessments are carried out to examine the effects of an agent on humans (Health Risk Assessment) and ecosystems (Ecological Risk Assessment). Environmental Risk Assessment (ERA) is the examination of risks resulting from technology that threaten ecosystems, animals and people. It includes human health risk assessments, ecological risk assessments and specific industrial applications of risk assessment that analyze identified end-points in people, biota or ecosystems.

Keywords: risk assessment, exposure, hazard and environment

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L.I. Simeonov and M.A. Hassanien (eds.), *Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology*,

1. Introduction

Environmental risk assessment refers to the quantitative and qualitative evaluation of the risk posed to human health and/or to the environment by the actual or potential presence and exposure to particular pollutants. The relationships between the sources, exposure and effects of contaminants to human and ecological receptors are the basis to risk assessment. Environmental risk tools are based on models that describe pollutant pathways in open environmental system and simulate or model the release of a hazard from a source to the environment. In the context of environmental pollution a site specific assessment is conducted to inform a decision concerning a particular location. As generic purpose it may determine appropriate soil cleanup levels at the site; establish water discharge permit conditions to meet regulation standards and investigate the need for emission standards for sources of hazard air pollutants (EPA, 2007). An accurate site-specific assessment requires knowledge of contaminant form and how it enters in the environment; environmental conditions affecting contaminant (meteorological conditions, soil chemistry, water and sediment chemistry, etc.); presence of plants or animals contaminant bioaccumulation; pathways and routes of exposure to human or ecological receptors and the effects of the contaminant in the target receptor (EPA, 2007). Risk assessments vary widely in scope and application. Some look at single risks in a range of exposure scenarios, others are site-specific and look at the range of risks originated by a facility (Fairman et al., 1998). In general, risk assessments are carried out to examine the effects of an agent on humans (Health Risk Assessment) and ecosystems (Ecological Risk Assessment). Environmental Risk Assessment (ERA) is the examination of risks resulting from technology that threaten ecosystems, animals and people. It includes human health risk assessments, ecological risk assessments and specific industrial applications of risk assessment that analyze identified end-points in people, biota or ecosystems (Fairman et al., 1998). Although health and ecological risk assessment are two different types of risk assessment, both processes are conceptually similar (in fact, ecological risk assessment was developed from human health risk assessment), but have a differing historical development, regulatory and policy priorities. Applied industrial applications have been separated as many of these assessments do not look in isolation at people or ecological systems. They look at real situations and they are likely to include engineering risk assessments as part of the overall environmental risk assessments and may take an integrated approach to human and environmental risks (Fairman et al., 1998). Although risk assessment is extensively used in environmental policy and regulation providing the scientific basis for much legislation and environmental guidelines, the results of risk assessment are not often universally accepted. This is mainly due to problems concerning the availability and quality of data used in risk assessment, the interpretation of data and results of the assessment as well as the treatment of uncertainty (Fairman et al., 1998).

2. Risk Assessment Methodology

More specifically, an environmental risk assessment is an analysis of the potential for adverse effects caused by contaminants of concern from a site to determine the need for remedial action or to develop target levels where remedial action is required. It involves analyzing the sources of a release, the mechanisms of chemical transport and the potential health risks to receptors. Usually risk analysis focus on three categories of risk problem: (i) source term risks: associated with the risk of an event occurrence that may result in a release to the environment (a landfill liner failure, inappropriate treatment of an effluent discharged in a stream, etc.); (ii) pathway risks: address the likelihood of a certain exposure of an environmental receptor to a hazard following an initial release (dispersion of a plume downwind of a stack, movement of a plume in groundwater towards to a receptor point, etc.); (iii) the risks to harm the receptor that might occur as a result of the exposure (adverse health effects as a result of exposure to hazard gaseous contaminants or drinking water polluted).

Often the methodology for exposure and risk assessment to environmental pollution is translated into sets of assessment questions throughout the several stages of risk assessment (planning and problem formulation, exposure analysis and interpretation and risk characterization) (EPA, 2007). These questions are used to meet the needs of assessment, particular important in focusing the assessment during the problem formulation.

The planning and problem formulation stage provides an opportunity for initial consideration of the contaminant characteristics and their chemistry. These considerations, along with other aspects of the assessment, contribute to the development of a conceptual model that gives the important elements of risk assessment. The next step should provide information about the exposure and the consequence effects. Tools and methods should be used to conduct a specific analysis of these two processes resulting in a receptor exposure assessment and a stressor dose–response assessment. Interpretation and risk characterization involves risk estimation, uncertainty analysis and risk description. The final step is communicating results to risk managers in order to carry out the risk management, by the application of the assessment results, to define management options and communicate them to the interested parties (EPA, 2007).

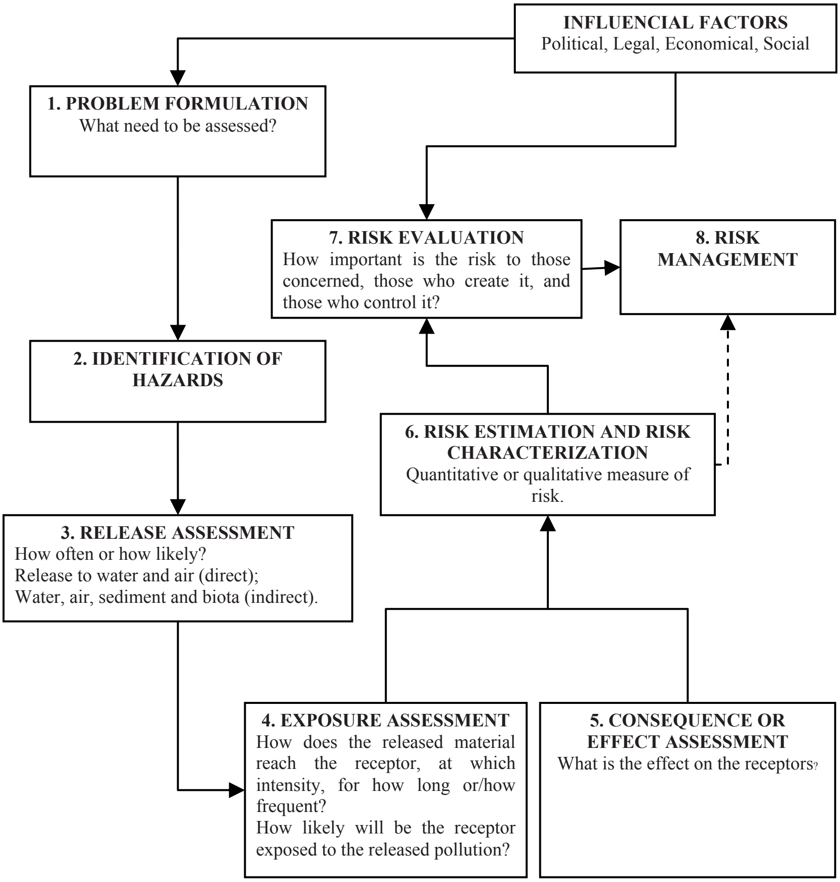

Figure 1. General key tasks in a environmental risk assessment. (From Fairman et al., 1998.)

There are several unifying principles underlying all risk assessments but to carry out a environmental risk assessment, six steps should be followed as guidelines (Fairman et al., 1998) (Figure 1):

i) Problem formulation (provides initial consideration of contaminant characteristics and their chemistry)
ii) Hazard identification (what chemicals are present and are they likely to be toxic?)
iii) Release assessment (sources and rate releases)
iv) Exposure assessment (who is exposed, at what concentration, how often and for how long?)
v) Consequence or effect assessment (how is it toxic and at what exposure levels and what is the effect on the receptors)

vi) Risk estimation and characterization (what does the risk assessment tell us about the situation and what are the risks, quantitative or qualitative)

Environmental risk assessment is also likely to include a seventh step given by risk evaluation defining how important is the risk to those affected, those who create it, and those who control it.

This step has laid down in the European legislation of new and existing substances (Fairman et al., 1998). The conclusions made in the risk characterization and/or risk evaluation are used as input for risk management in order to come up with an answer to which actions should be taken and how should the remaining risks be handled. Each one of this step will be discussed in detail in the following sections.

2.1. PROBLEM FORMULATION

In the first step the problem must be formulated and certain tasks must be clear before the assessment proceeds. These tasks should be based on (EPA, 2007): "What are we actually attempting to assess? What is the risk source? Is it a single chemical, an industrial plant or a process such as transportation? Are we concerned with the production, use or disposal of the hazard?" The risk source will generate hazards that may be released into the environment contributing to the transport, transfer and fate processes through the atmosphere, subsoil, underground and superficial aquatic systems, leading to the contamination of new environmental sub-compartments.

Also one should be point out the reasons why we are carrying out the risk assessment; which hazards should we include in the assessment; if it is based on regulatory standards to determine the "acceptable risk" or if regulatory and policy frameworks are being used to identify the most relevant end-points (EPA, 2007). During the problem formulation stage the following planning and scoping activities should also be included (EPA, 2007):

- Define the geographic scale and scope of the assessment.
- Identify potentially exposed populations and sensitive subpopulations.
- Characterize exposure pathways and exposure routes that will represent the conceptual model.
- Describe how exposure will be assessed.
- Determine how the hazard and the receptor's dose–response will be assessed.
- Describe how risks will be characterized.

2.2. HAZARD IDENTIFICATION

Hazard identification involves the identification of those agents that could possibly cause harm to the receptor (people, organisms or ecosystems), specifying how this harm could occur.

The methods by which hazards are identified depend on the nature of the hazard and may include toxicological testing, examination of accident rates and epidemiological studies. There is a wide range of hazard identification techniques used in all types of risk assessment, but in particular for industry the most applicable resume to four of these techniques (Fairman et al., 1998):

- *What if* technique: brainstorming examinations of a process or a procedure, carried out in a small team with a chairman asking questions. The analysis considers the results of unexpected events that would produce an adverse consequence.
- *Checklists* technique: specify those components of a plant which requires a safe design. This technique uses data from industry, past accidents and expert judgements.
- *Fault trees analyses*: diagram that illustrates combinations of failures that will cause one specific failure or interest, the "top event"; the root is the main event and possible causes of the event are traced back to several initiating events.
- *Event trees analyses*: evaluates the potential for an accident as the result of a general equipment failure or process malfunction, known as the initiating event.

The hazard identification in the environment will include the phases of sampling and analyses to determine if the chemical may be toxic, to model the chemical fate and transport, to know how the contaminant or chemical may move through the environment to develop a conceptual site model, organize information regarding contaminants and chemicals and potential transport to people. For the conceptual model several inputs will be needed in order to gather information about the transport of contaminants and chemicals, the target exposed population and the way exposure changes in time. At last, we should analyse what information is missing; this last step is important to evaluate how realistic is the conceptual site model. In summary, the conceptual model lays out a series of working hypotheses about how the contaminant(s) of concern might move through the environment to cause adverse effects in humans or ecological systems. These hypotheses are examined through data analyses, models or other predictive tools, to determine the probability and magnitude of the occurrence of unwanted effects.

2.3. RELEASE ASSESSMENT

A release assessment involves the identification of the risk potential source to introduce hazardous agents into the environment. This may be descriptive or involve the quantification of the release. It should identify the types of releases, its mechanism, the amount released, timings and probabilities of the release occurrence and a description of how these attributes might change in space and in time as a result of various actions or events (Fairman et al., 1998). The likelihood or probability of a release of hazards in a non-quantitative way may be given by "Expert judgment"; based on the results of the hazard identification. The likelihood is divided in different categories in terms of expressions such as: likely, may occur, not likely and very unlikely (Wilcox et al., 2000).

2.4. EXPOSURE ASSESSMENT

Exposure assessment is probably the most variable aspect of the risk assessment process. This is the reflection of a variety of contributing factors such as several exposure pathways, the unique nature of ecosystems, fauna and flora together with differing methodologies for exposure assessment as well as differences in dose response extrapolation methodology; for all these reasons, the exposure assessment is a critical element of the risk assessment (EPA, 2007). The assessment phase is the process of estimating exposure and understanding the dose–response relationship between the receptor and the contaminant. It should include a description of intensity, frequency and duration of exposure through the various exposure compartments, routes of exposure and the identification of the potential receptors exposed and a prevision of how these factors might change as a result of various actions or events and also with time. The exposure assessment step requires the use of monitoring data, exposure modelling techniques and also mapping models. Most of the time, exposure is determined in terms of the predicted environmental concentration, which is calculated on both local and regional spatial scales from monitoring data, when available, or by using realistic worst-case scenarios. If this information is not available, estimative may result from exposure models. Dispersion modelling is one approach to quantify the spatial extent of exposures to the wider environment from a point or area source.

The data and models used should be critically examined to ensure that they are appropriate to the level of the assessment results. The aim of this stage is to produce a complete picture of how, when, and where the exposure occurs or has occurred, by evaluating sources and releases and the extent and pattern of contaminant contact with humans or ecologically relevant biota.

As a check procedure for this step, we should be able to answer to these questions: who is exposed? (is it an adult, a child or special populations with special characteristics?); how are they exposed? (is it through ingestion, inhalation or skin contact?); what is the concentration of chemical to which they are exposed in air, water or soil?; how often are they exposed? (days per year and the number of years exposed).

2.5. CONSEQUENCE OR EFFECTS ASSESSMENT

A consequence assessment analyzes the effects of the release or the production of the hazards to the specified receptors, and it involves quantifying the relationship between specified exposures to the hazard, health and the environmental effects of those exposures. The effects examined for human health are usually mortality or morbidity. The effects observed in ecological systems are much more varied and few defined end-points exist at present. The data for consequence assessment are mostly based on toxicity and ecotoxicity testing, epidemiology and dose–response models (Fairman et al., 1998). A dose–response curve will give the relationship between the exposure to (or intake of) a hazardous agent and its toxicological (or chemical, or physical) effect on the receptor.

The consequence assessment should describe how the effects are elicited, link them to the receptor at greatest risk and evaluate how they change with varying exposure levels. The analysis addresses the veracity that effects may occur or are occurring as a result of exposure to the contaminant of concern, and that linkages between measured effects and assessment endpoints can be made (this is especially important for ecological risk assessments).

Taken as example an ecological assessment, the consequences or effects can be estimated in terms of the Predicted No Effect Concentration (PNEC) (based on EC Directive 93/67/EEC). Different PNEC values need to be derived for the relevant compartments of interest (water, sediments and biota compartments). Ecotoxicity tests will generate the PNEC values. The ecotoxicity available data are used to derive a No Observed Effect Concentration (NOEC) or a Lowest Observed Effect Concentration (LOEC) (Fairman et al., 1998).

As a check procedure during this step, we should be able to answer to these questions: What toxicity data are available? Acute or chronic effect? Or both? Does it have a carcinogenic or a non-carcinogenic effect? Or both? We should consider the effects of multiple chemicals (multiple nonlethal effects can still have an adverse impact on human health) and consider the route of exposure (effects can be "route of exposure" specific).

2.6. RISK CHARACTERIZATION AND ESTIMATION

Risk characterization and estimation consists of integrating the results from the release assessment, exposure assessment and consequence assessment to produce measures of environmental risks. It is the final phase of the risk assessment and is the culmination of the planning, problem formulation and analysis of predicted or observed adverse effects. This may include an estimate of how many individuals experienced the health effects over time or measures indicating environmental damages as well as the uncertainty involved in these estimates; it should include and report an uncertainty analysis (Fairman et al., 1998).

The process of interpreting and integrating the information on hazard and exposure to provide a practical estimate of risk is complex and may involve determining what an acceptable risk is and how risk should be managed. As a check procedure during this stage we should be able to know what is the likelihood of harm following exposure to this contaminant or chemical in this specific situation, identify the receptors and exposure pathways of most concern, provide a numerical estimate of risk, identify key uncertainties in this estimate and compare the numerical estimate of risk with a previously determined risk goal.

We also should be aware of what does risk assessment not tells us such as whether risk is "acceptable", whether risk is equitably distributed across population or predictions regarding personal or individual risk.

Risk assessment is one part of a decision making process to manage hazards; science determines likelihood of effect but risk management determines whether and how the risk should be addressed; it is a decision making process to determine whether to take action for an identified risk.

The European Union practice on risk characterization involves the calculation of the PEC/PNEC ratio which should be calculated for all relevant endpoints. If the PEC/PNEC is less than 1, the substance of concern is considered to present no risk to the environment and there is no need for further testing or risk reduction measures. But if this ratio cannot be reduced to below 1 by refinement of the ratio (by gathering of further information and further testing), risk reduction measures are necessary (Fairman et al., 1998).

Sometimes a quantitative risk assessment approach can not be carried out (no PEC or PNEC can be properly calculated). In these cases, a qualitative risk assessment can be used as an alternative in which the risk characterization shall include a qualitative evaluation of the likelihood that an effect will occur under the expected conditions of exposure. These results can be used as a base to prioritize risk reduction measures (Fairman et al., 1998).

2.7. RISK EVALUATION

Risk evaluation represents the evaluation of what risk assessment actually means in practice. What is the significance or value of the identified hazards and estimated risks? Risk evaluation deals with the trade-off between the perceived risks and benefits. This will include the public perception of the risk and the influence that this will have on the acceptability of risks decisions; it may take account of these perceived risks and benefits and incorporate them in the final risk assessment. On its turn, the public perception of risk depends on the economic, social, legal and political context in which the affected and/or concerned population lives (Fairman et al., 1998). The results from this risk evaluation may serve as an input to the risk management process. Based on the acceptable level of risk, eventual choices of action are determined to achieve the desired level of risk; if a system has a risk value above the risk acceptance level, actions should be taken to address concerned risks and to improve the system though risk reduction measures. Risk management decisions or actions may result in: (i) no action at all, (ii) implementation of information programmes; (iii) economic incentives; (iv) establish ambient standards; (v) pollution prevention; (vi) chemical substitution and/or chemical ban.

2.8. UNCERTAINTY

Uncertainty is inherent to all risk assessments. It is important to assess the magnitude of the uncertainty to determine the "relevance" of the quantified risk. Risks associated with a specific risk source and receptor, under pre-specified surrounding conditions, will be expressed in terms of a range (with a lower and upper bound) rather than a single figure. Knowing the uncertainty is also important to ensure that the input of the results into the risk evaluation step is realistic and thus to ensure that appropriate risk management decisions are made (Calewaert, 2006). Uncertainty can arise from several potential sources (Calewaert, 2006):

- Uncertainty inherent to methods used in each of the ERA steps: choice of model, assumptions made in used models, uncertainties related to the model structure itself as the lack of confidence that the mathematical model is an adequate representation of the assessment problem
- Uncertainty related to the collected data and parameters: gaps in historic/recent data, use of data from other situations and extrapolations to fill out gaps, variability of a model parameter from its true heterogeneity over space and time, uncertainty of a model parameter resulting from the lack of information or knowledge about its true value

- Uncertainty of the analyst: interpretation of ambiguous or incomplete information, human error, uncertainty of how an assessor translates a real or forecasted situation in a given model

Quantifying all sources of uncertainty is difficult. Methods for estimating the uncertainty are for example statistical analysis (for uncertainty related to data and parameters models), expert judgment (for uncertainty related to models) and sensitivity analysis (for uncertainty related to future trends). Uncertainty should be assessed for each one of the ERA steps.

3. Risk Assessment Application to a Case Study

3.1. APPROACH OVERVIEW

This section describes the methodology applied to calculate lifetime cancer incidence risk and non-carcinogenic health effects resulting from exposure to radionuclides and chemicals released from a contaminated site during a certain period of time. This approach uses current measures of radionuclides and chemicals in the environment media that individual members of the public may come in contact with, or be exposed to, during their daily activities while living near by the contaminated site. Radionuclide or chemical intake by humans is calculated using the average concentrations at the exposure site and applying typical intakes, such as a breathing rate or a water ingestion rate, associated with appropriate exposure parameters.

Carcinogenic risk or non-carcinogenic effects are estimated by multiplying the radionuclide or chemical intake or exposure, by the respective cancer risk or health-effects factor that relates the human risk to the amount of hazardous substances that the receptor takes into the body. This refers to a specific exposure period, therefore concentrations used for the radionuclide and chemical in environmental media should represent the exposure concentration over the same period of time considered.

A generic environmental media in which humans may be directly exposed or may generate an indirect exposure are: (i) Air; (ii) Groundwater; (iii) Surface water; (iv) Soil (surface and subsurface); (v) Sediments; (vi) Fish; (vii) Food crops (leafy and non-leafy, vegetables, grains, fruits); (viii) Vegetation (mainly pasture grass) and (ix) Animal products (milk, meet, eggs, etc.) (EPA, 1998).

The methodology requires concentrations of radionuclides and chemicals in air, surface water, and groundwater and, in some cases, in soil and sediments. These concentrations may represent measured or modeled values. Models developed previously were used to estimate radionuclide or chemical concentrations in soil and biota, as well as concentrations in vegetation and in milk, from radionuclide or chemical concentration in air, surface water and groundwater. The endpoints of this approach is the annual incremental lifetime excess carcinogenic risk and a hazard quotient based on the annual non-carcinogenic effects for persons living, working and recreating in the model domain or in the study area for the a given exposure period (Rood, 2003).

The risks and health effects are calculated separately for each individual source of radionuclides and chemicals. This approach is designed to be general in nature and capable of considering almost any exposure scenario. Not all pathways included in this study may be important in terms of risk. However, the approach should be able to address each pathway quantitatively in order to assess its potential importance in terms of overall risk. Intake and exposures implicit refer to the various locations of exposure as well as to the fraction of time spent at each location. Risk from each exposure medium is calculated separately and then summed across all exposure media, exposure pathways and materials of concern. Risks are also summed separately for radionuclides, carcinogenic chemicals and non-carcinogenic chemicals. The final risk value is then determined.

This example intends to focus on the risk assessment methodology; the exposure models have been developed and published already (Dinis and Fiúza, 2005, 2006, 2007). Exposure scenarios definitions, exposure scenario parameters and parameters specific to radionuclides and chemical transport in soil and biota are not covered in this study.

3.2. SITE CHARACTERIZATION

As a reference site to apply the risk assessment methodology, a contaminated site from a former Portuguese uranium mine was selected. This mine was located in the central part of Portugal and it was exploited for almost a century, first for radium production (1913–1944) and then for uranium concentrates production (1951–2000). The mine is surrounded by small houses and country houses, with most of the local population living in a village within about 2 km from the mine. A tailing disposal is located near the mine; the liquid effluents, after neutralization and decantation, were discharged into a streamlet (Pantanha) flowing to the Mondego river (Bettencourt et al., 1990).

The contaminated site represents an area of 13.3 ha and until a very recent past radionuclides and chemicals have been released to the air, soil, surface water and indirectly to groundwater as a result of routine operations, accidents and waste disposal practices. Presently, a rehabilitation plan based on an in-situ reclamation scheme to promote the confinement of the tailings materials is under implementation as well as a wastewater treatment system implemented in the mining area (Nero et al., 2005).

3.3. ENVIRONMENTAL MEDIA CONSIDERED

An environmental medium is defined as a discrete portion of the total environment that may be sampled or measured directly such as soil, sediment, groundwater, surface water or air (Rood, 2003). Environmental media considered in this study that humans may be exposed or consume are: Air; Groundwater; Soil; Food crops; Animal products.

3.4. EXPOSURE ROUTES

An exposure route is the manner through which a material of concern comes into contact with a human receptor (Rood, 2003). Exposure routes that may be considered in this methodology are: Inhalation; Ingestion; Dermal contact with soil and water; Irradiation from air; water, soil and dry sediments (radionuclides only).

3.5. EXPOSURE PATHWAYS

An exposure pathway is the course that a substance of concern takes from its source (where it began) to its end point (where it ends), and how people can come into contact with (or get exposed to) it. An exposure pathway can be divided in five simpler components: (i) a source of contamination (such as an abandoned facility); (ii) an environmental media and transport mechanism (such as movement through groundwater); (iii) a point of exposure (such as a private well); (iv) a route of exposure (eating, drinking, breathing, or dermal contact), and (v) a receptor population (people potentially or actually exposed). When all five parts are present, the exposure pathway is termed a completed exposure pathway. All exposure pathways begin with a release from a source to an environmental medium. Sources are related to releases, discharges, or disposal to air, water and soil or sediment. These sources can contribute with materials of concern to four transport media (air, infiltrating and saturated groundwater, surface water) and three static media (surface soil, fluvial sediment and subsurface soil). A transport media is an environmental medium where transport (advection, dispersion) and transfer (sorption, deposition, resuspension) processes are applied. A static medium is defined as an environmental medium where only transfer processes occur (Rood, 2003).

The following components of the exposure may be considered in this methodology:

- **Source term:** Atmospheric releases; Solid waste (tailings); Liquid waste (effluents).

- **Environmental media:** Air (physical transport as advection and dispersion); transfer between media can occur – transport media; Surface soils (transfer between media can occur but transport within the medium is not considered – static medium); Animal products (environmental medium for biota; transport within the media is not considered).
- **Human exposure routes:** Ingestion; Inhalation; External radiation; Immersion; Dermal contact.
- **Transfer processes:** Deposition; Leaching; Irrigation; Ingestion by animals; Resuspension; Root uptake; Sorption (adsorption + absorption); Surface runoff; Biota transfer processes (absorption + translocation); Volatilization; Weathering.

The intake or exposure from each exposure route is multiplied by an appropriate factor relating intake or exposure to risk. The sum of risk from all exposure routes yields the total risk incurred from all exposure pathways considered for each substance of concern (Ingestion + Inhalation + Immersion + Dermal contact + External radiation = Total risk).

3.6. CONCENTRATIONS AT POINTS OF EXPOSURE IN EACH ENVIRONMENTAL MEDIA AND EXPOSURE SCENARIO DEFINITION

As a starting point it is assumed that there are measured or modeled concentrations of radionuclides and chemicals in environmental media. Concentrations in air, surface water or groundwater transport media are required. Transfer of radionuclides and chemicals from a transport media to static media (soil and biota) were performed in the modeling work developed before and published (Dinis and Fiúza, 2007). Concentrations are averaged over the exposure period and are intended to represent contributions from the contaminated site only. The exposure scenario is composed by a group of exposure pathways that define: (i) location of points of exposure, duration of exposure and the individual reside, works, or activities in the study area; (ii) environmental media that the individual contacts with and (iii) estimate the quantity that is taken from the media into the body or that comes in contact with the body (Rood, 2003). The location may be defined in terms of a point coordinate. In this point, the receptor may breathe contaminated air, receive external exposure from gamma-emitting radionuclides in soil, fluvial sediments, consume water from a private well water supply, intentionally or unintentionally consume surface water, intentionally or unintentionally ingest contaminated soil, have contact direct with contaminated soil or be immersed in contaminated surface water or groundwater. Additionally, the receptor may consume homegrown garden products or milk from a backyard cow.

Generically, some basic assumptions, limitations and principles involve the definition of all exposures pathways that make up the exposed scenarios. The mainly assumptions are:

- Receptor's daily activities occur in the study area (lives, work and recreates).
- The receptor may consume water from a private well; groundwater or surface water may also be used to irrigate crops and livestock.
- Risks endpoints include carcinogenic risk and non-carcinogenic effects calculated and discussed separately for radionuclides and chemicals according to the respective exposure pathway. Specific health-effects estimates include: incremental lifetime cancer incidence risk from radionuclides; incremental lifetime cancer incidence risk from chemicals and non-carcinogenic effects from chemicals.
- The total risk calculated represents the risk originated from the considered exposure period.

Generally, equations of cancer risk and non-cancer effects are set in terms of total risk. For this study, however all components of cancer risk or non-cancer effects are calculated and discussed separately.

In the following sections only some of the possible exposure pathways will be covered. Also different scenarios will be considered to show how to calculate the risk in different exposure scenarios.

3.7. RISK CALCULATION

For each of one of these cases we will consider only the internal exposure by inhalation and ingestion. No external exposure due to external radiation was considered. For internal exposure the total risk will be the sum of the risk by inhalation, soil ingestion, water ingestion and foodstuff ingestion. The contaminants of concern considered are radon (Radon-222), radium (Radium-226), arsenic (inorganic As) and beryllium (Be).

We adopted as an acceptable risk the values below a Health Quotient (HQ) of 1 for non-carcinogens and below an Incremental Lifetime Cancer Risk (ILCR) of 1 in 1,000,000 for carcinogens (10^{-6}) (EPA, 1995).

3.7.1. *Incremental Lifetime Cancer Risk Incurred by Radionuclides Exposure*

3.7.1.a. Radon Inhalation

Radon-222 is a radioactive gas released during the natural decay of thorium and uranium, which are naturally occurring elements found in varying amounts in rock and soil. Radon-222 decays into radioactive elements, two of which, polonium-218 and polonium-214, emit alpha particles, which are highly effective in damaging lung tissues. These alpha-emitting radon decay products have been implicated in a causal relationship with lung cancer in humans. Lung cancer due to inhalation of radon decay products constitutes the only known risk associated with radon. However, not everyone exposed to elevated levels of radon will develop lung cancer, and the amount of time between exposure and the onset of the disease may be many years. Outdoors radon poses significantly less risk than indoors because it is diluted to low concentrations and dispersed in the air. In the indoor air environment, however, radon can accumulate to significant levels. Reduced ventilation may enable radon and its decay products to reach levels that are orders of magnitude above the outdoors levels. The magnitude of radon concentration indoors depends primarily on a building's construction and the amount of radon in the underlying soil. Many large scale studies have been conducted throughout the world to assess the indoor radon problem. In most common scenarios, the inhabitants go to work in day time so windows and doors are kept closed during this period. In the contaminated site considered there are several cases of houses constructed with mining waste material leading to high radon indoor levels. Radon in indoor air was measured in homes near the site and radon concentrations in the outside air were measured in the vicinity of the contaminated site (Falcão et al., 2005).

The critical receptor considered in this study is represented by farmers from the small farms in the vicinity of the site, for whom time not spent in their houses is likely spent outdoors; the following scenario suppose that the receptor spend 12 h/day during all year inside the house and 8 h/day, 5 days/week, outdoor working in open-air farm activities. The expression to estimate the cancer risk incurred by indoor radon inhalation is ($R_{Rair,inh}$) (Rood, 2003):

$$R_{Rair,inh} = C_{air} \cdot BR \cdot RC_{air,inh} \cdot E_f \cdot f_{eq} \tag{1}$$

where C_{air} = 381 Bq/m^3 (Falcão et al., 2005) is the radon concentration in the indoor air; BR = 17.8 m^3/day is the inhalation or breathing rate at the exposure location (EPA, 1999); $RC_{air,inh} = 4.86486 \times 10^{-10}$ Bq^{-1} is the cancer slope factor for radon inhalation (EPA, 1995); E_f = 183 days/year is the indoor exposure frequency and f_{eq} = 0.4 is the equilibrium factor for radon decay products (EPA, 1997).

The resulting annual cancer risk from indoor radon inhalation is 2.42×10^{-4}. This shows that indoor radon poses a risk of 1 in 10,000 (10^{-4}). This value can be multiplied by 75 years to calculate the lifetime risk of lung cancer (ages 40–85) which yields 0.018 (Khan, 2000). To estimate outdoor radon inhalation risk we should use the radon outdoor concentration, C_{air} = 122 Bq m^3 (Falcão et al., 2005) and an outdoor exposure frequency of 87 days/year (8 h/day, 5 days/week, 52 weeks/year) in the above equation. The resulting annual cancer risk from outdoor radon inhalation is 3.68×10^{-5}. This corresponds to a lifetime risk of lung cancer for an average life expectancy of 75 years of 0.003 (EPA, 1997).

3.7.1.b. Radium-226 Ingestion (Soil, Drinking Water, Food Products: Leafy Vegetables and Milk)

The risk will be due to the ingestion of radium-226 present in soil, drinking water and food products such as cow's milk and leafy vegetables.

For contaminated soil, the route of exposure is via incidental soil ingestion. The expression to calculate this risk is given by ($R_{Rsoil,ing}$) (Rood, 2003):

$$R_{Rsoil,ing} = C_{soil} \cdot U_{soil,ing} \cdot RC_{soil,ing} \cdot E_f \tag{2}$$

The necessary inputs to calculate the resulting risk are: soil concentration, C_s = 257 Bq/kg (Pereira et al., 2004); soil ingestion rate (adult agriculture scenario) $U_{soil,ing}$ = 100 mg/day or 0.0001 kg/day (WISE, 2004); risk coefficient for soil ingestion, $RC_{soil,ing} = 1.97027 \times 10^{-8}$ Bq^{-1} (EPA, 1995) and exposure frequency, E_f = 87 days/year. The resulting annual cancer risk incurred by soil ingestion is 4.41×10^{-8}. For a long-term chronic ingestion of soil contaminated with radium-226 during 75 years (EPA, 1997) the incremental lifetime cancer risk is 3.30×10^{-6}. This show that soil ingestion contaminated with radium does not pose any extra risk. Well water contaminated with radium-226 will pose a risk by ingestion based on the following scenario: all drinking water to the receptor is supplied by water taken from a well located hydrologically downgradient from the tailings pile. The expression to calculate this risk is given by (Rood, 2003):

$$R_{Rwater,ing} = C_{water} \cdot U_{water,ing} \cdot RC_{water,ing} \cdot E_f \cdot f_{water} \tag{3}$$

Radium concentration in the well water is given by C_w = 0.4 Bq/L (EXMIN, 2003); water ingestion rate, $U_{water,ing}$ = 2 L/day (EPA, 1997); risk coefficient for water ingestion, $RC_{water,ing} = 1.04054 \times 10^{-8}$ Bq^{-1} (EPA, 1995); the fraction of contaminated water used for drinking (f_{water}) was assumed to be equal to 1 (i.e., all drinking water available for consumption at a site is potentially contaminated), thus, it was assumed that the receptor gets 100% of their drinking water from groundwater; exposure frequency (E_f) was set to 365 days/year, assuming that the receptor does not take any vacation time away from their homes ever. In case of a residential scenario it should be considered an exposure frequency of 350 days/year according to EPA Human Exposure Factors policy (EPA, 1997), assuming that residents take an average of 2 weeks' vacation time away from their homes each year.

The annual cancer risk incurred by water ingestion is 4.56×10^{-6}. For a long-term chronic ingestion of radium-226 during 75 years the incremental lifetime cancer risk is of 3.42×10^{-4} which means an incremental risk of 1 in 10,000.

Consumption of locally grown food products from small farms around the tailings and the mine may be contaminated with radium-226 by irrigation with contaminated water (from the well or from the streamlet) or by airborne particles from the tailings. It should be considered the consumption of vegetables (potatoes, tomatoes, carrots, etc.) and leafy vegetables (lettuce, cabbage, broccoli, etc.) grown in these farms but only leafy vegetables (mainly cabbage) were considered due to the available data. Milk consumption from farm cows was also considered. The risk resulting from the ingestion of contaminated leafy vegetables is (Rood, 2003):

$$R_{Rveg,ing} = C_{veg} \cdot U_{veg,ing} \cdot RC_{veg,ing} \cdot E_f \cdot f_{veg} \qquad (4)$$

Radium-226 concentration measured in leafy vegetables (C_{veg}) was 21.9 Bq/kg (Falcão et al., 2005); vegetation ingestion rate ($U_{veg,ing}$) was set to 0.175 kg/day (Yu, 2001); risk coefficient for foodstuff ingestion ($RC_{food,ing}$) was considered to be 1.38919×10^{-8} Bq^{-1} (EPA, 1995); exposure frequency (E_f) was set to 365 days/year, as previously, and the fraction of ingested leafy vegetables from the farm products (f_{veg}) was set to 1 (all leafy vegetables consumption comes from the farm and are contaminated). The cancer risk incurred by contaminated leafy vegetables ingestion is 1.94×10^{-5}. For a long-term chronic exposure corresponding to an average life expectancy of 75 years, the incremental lifetime cancer risk is 1.46×10^{-3} (EPA, 1997). This means an excess risk of 1 in 1,000.

Cow's milk contamination is due to both animal's ingestion (contaminated water, soil and pasture) and inhalation. The risk is estimated by the same expression as for leafy vegetables consumption with the following inputs: milk concentration, C_{milk} = 0.029 Bq/L (modeled for a similar contaminated site) (Dinis and Fiúza, 2007); milk ingestion rate, $U_{milk,ing}$ = 0.615 L/day (EPA, 1997); risk coefficient for milk ingestion, $RC_{food,ing} = 1.38919 \times 10^{-8}$ Bq^{-1} (EPA, 1995); exposure frequency, E_f = 365 days/year and considering that all ingested milk comes from the farm cows and is contaminated, $f_{milk} = 1$. The annual cancer risk incurred by milk ingestion is 9.04×10^{-8}. For a long-term chronic exposure period of 75 years the incremental lifetime cancer risk is 6.78×10^{-6}. This value does not pose any extra risk incurred by the ingestion of milk contaminated with radium-226. The total incremental cancer risk incurred by the ingestion of contaminated soil, water, leafy vegetables and milk is 1.81×10^{-3}, which means an excess risk of 1 in 1,000 mainly due to leafy vegetable ingestion and water ingestion. The total incremental lifetime risk cancer resulting from inhalation and ingestion is 2.72×10^{-2}.

3.7.2. *Incremental Lifetime Cancer Risk Incurred by Chemical or Metal Exposure*

Arsenic present in drinking water from the water well was considered for this exposure pathway. Some authors reported that the health effects from ingestion of 1–2 mg/kg/day of inorganic arsenic result in nausea and vomiting followed by severe abdominal pain, bleeding in the gastrointestinal tract, and in some cases, death by renal failure (ATSDR, 2008). Levels of arsenic substantially above this level in current drinking water, if ingested daily over many years, could cause the chronic arsenic poisoning.

The incremental lifetime cancer risk incurred by a person ingesting contaminated water with arsenic is computed for a single carcinogenic chemical or metal by this expression (Rood, 2003):

$$RC_{water,ing} = C_{water} \cdot U_{water,ing} \cdot \frac{SF_{water,ing}}{BW \cdot AT} \cdot E_f \cdot E_d \tag{5}$$

Arsenic concentration in well water, C_{water} = 0.143 mg/L (EXMIN, 2003); water ingestion rate, $U_{water,ing}$ = 2 L/day; cancer slope factor for arsenic ingestion in drinking water, $SF_{water,ing}$ = 1.5 (kg day)/mg (IRIS, 2008); body weight, BW = 70 kg; averaging time AT = 75 years (or 25,550 days, life expectancy); exposure frequency, E_f = 365 days/year; exposure duration E_d = 30 years. The incremental lifetime cancer risk for an individual who consumed 2 L of water per day at 0.143 mg/L of arsenic during 30 years is 0.002627 or 2.63×10^{-3}, which means an excess risk of 1 in 1,000.

3.7.3. *Noncarcinogenic Health Effects Incurred by Chemical or Metal Exposure*

Beryllium concentration in soil may lead to windborne or airborne particulates contaminated. Inhalation of beryllium may result in rhinitis, tracheobronchitis, pneumonitis and death due pulmonary edema or heart failure. It can mainly result into two types of respiratory disease, acute beryllium disease and chronic beryllium disease (berylliosis). Both forms can be fatal. Chronic beryllium disease results from breathing low levels of beryllium and is a type of allergic response. There can be a long latency period (up 25 years following exposure) prior to the onset of any symptoms. The health effects incurred by beryllium inhalation may be estimated by the expression (Rood, 2003):

$$HQ = \frac{C_{air} \cdot BR \cdot E_f \cdot E_d}{R_f D_{inh} \cdot BW \cdot AT} \tag{6}$$

Noncarcinogenic health effects are quantified in terms of hazard quotient (HQ) evaluated for a possible receptor exposed to beryllium by inhalation: an exposure scenario of 8 h/day, 5 days/week, 52 weeks/year, corresponding to 87 days/year of exposure frequency (E_f) to soil contaminated with beryllium was considered in this study. The other necessary inputs are: Beryllium concentration in air, $C_{air} = 1.09 \times 10^{-5}$ mg/m^3 (estimated from available data); breathing rate, BR = 17.8 m^3/day; body weight BW = 70 kg; averaging time AT = 75 years or 25,500 days; exposure frequency E_f = 87 days/year; exposure duration E_d = 30 years and the beryllium reference dose for inhalation (R_fD_{inh}) is 5.7×10^{-6} mg/(kg day) (EPA, 1995). The resulting hazard quotient to quantify the noncarcinogenic health effects incurred by beryllium inhalation is HQ = 0.05 which is inferior to one; the exposure to beryllium in this scenario does not pose any risk.

4. Discussion and Conclusions

The focus of this study was to exemplify how to apply a risk assessment in some of its components. More specifically it was intended to evaluate the potential impacts of current releases of hazardous substances from a contaminated site with uranium tailings and wastes during almost a period of 30 years. Several scenarios could have been adopted for different exposure pathways or routes of exposure. A life expectancy of 75 years was assumed to carcinogenesis effects. Radionuclide and chemical concentration in soil, air and groundwater, were needed along with parameters describing the exposure scenario. Radionuclide in leafy vegetables was measure but cow's milk concentration was modeled from pasture ingestion contaminated by soil, air and groundwater in an appropriate exposure scenario (Dinis and Fiúza, 2007).

The exposure pathways included in this risk assessment represent some of the exposure pathways that may be present in a contaminated site with radioactive materials and heavy metals; however is not an exhaustive list of potential exposure pathways.

From the results obtained it can be concluded that most of incremental lifetime cancer risk incurred by radionuclides exposure is due to indoor radon inhalation. In a risk management stage the risk manager could propose some mitigation measures to minimize the exposure and, in this way, decrease the risk. Some of these measures are easy to handle such as sealing cracks and other openings in the house's foundation, installing a vent pipe system and fan, which pulls radon from beneath the house and vents it to the outside (soil suction radon reduction system), promote ventilation (artificial or natural) inside the houses, specially in the lower floors and install continuous electronic radon monitors or alpha-track (ATD) detectors to control radon levels, making periodic long-term measurements to insure that the system continues to reduce the radon to acceptable levels.

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RISK ASSESSMENT APPROACHES FOR DEALING WITH UNUSUAL CHEMICALS AND NON-STANDARD EXPOSURES

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Abstract. It is estimated that there are approximately 70,000 chemicals used in commercial activities. Robust toxicological data, such as would be suitable for risk assessment, are available for only a small fraction of these chemicals. While this lack of toxicity data is being addressed by recent governmental efforts such as the REACH program in Europe, data development will take considerable time. In addition, there are chemicals not covered by these regulations (e.g., process chemicals) which may nonetheless be involved in accidental exposures. Likewise, unusual exposure pathways may be of concern that are not addressed by standard exposure assumptions. Risk assessors and regulators therefore need to be open to creative and flexible approaches for dealing with such situations. Two case examples are discussed which illustrate these potential challenges and identify some possible solutions. First, we consider the case of an industrial accident which resulted in community exposure to a chemical synthesis intermediate for which toxicity data were lacking. Using a Structure Activity Relationship approach, a surrogate chemical for which toxicity data were available was identified. This allowed for estimation of potential health risks for the affected community. In the second example, we consider an occupational scenario where workers received dermal exposures to chemicals present in newly synthesized polyurethane foams. Standard exposure assessment algorithms were not sufficient for evaluating this exposure. Situation-specific information was used to estimate the transfer of the chemicals from the foam surface/subsurface to the workers' skin with subsequent dermal absorption. While uncertainties were inherent in this exposure assessment approach, they were believed to be small relative to the overall margin of safety indicated in the final assessment. The results of this assessment were used to guide the design of a worker protection program. These two case examples illustrate some of the challenges practitioners of risk assessment face as risk assessment

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becomes ever more widely used. They also demonstrate the need to promote flexibility and creativity in the risk assessment process.

Keywords: risk assessment, exposure pathways, structure activity relationships, modeling

1. Introduction

Although its roots reach back to at least the 1950s (Dourson et al., 1996; IOM, 2001), risk assessment truly developed into a widespread regulatory tool in the U.S. beginning in the 1980s. As part of that development process, the methodology for conducting risk assessment has undergone considerable codification and standardization. Thus, since the mid-1980s, risk assessment has been viewed in the U.S. as consisting of four distinct phases (i.e., hazard identification, exposure assessment, dose–response assessment, and risk characterization) each involving a number of specific steps (NRC, 1983). Methods for evaluating toxicity data and developing toxicity criteria have also been specified (U.S. EPA, 1986a, 1986b, 1989, 1991, 1994, 1996, 1998, 2004). With respect to environmental chemical exposures, various standardized formulae and exposure parameters have also been developed and agreed upon which address the major exposure routes (ingestion, inhalation, dermal absorption) to environmental media (air, water and soil/dust) (U.S. EPA, 1989, 1997a, 2004). This standardization process was highly desirable and in fact necessary in order to make risk assessment more transparent, decisions based on risk assessment more defensible, and to allow for comparability of results across different risk assessments. However, one potential downside of this process is that risk assessment has become, for some, a ‘cookbook’ process where all that is necessary is perfunctory application of the specified formulas and calculation of the resulting risks. This way of thinking obviously becomes problematic when conditions do not fall within the range contemplated by the available guidance. In such situations, risk assessors do not have the luxury of simply saying “there are no data (or applicable exposure formulas) and therefore we can do nothing” since in the environmental arena “taking no action” is an action itself.

In terms of dose–response assessment, it is important to note that only a very few of the estimated 70,000 chemicals in commerce have actually been tested for toxicological effects and even fewer have had toxicity criteria established (Clements et al., 1993). For example, the U.S. Environmental Protection Agency’s Integrated Risk Information System (IRIS) website provides verified toxicity values for just 544 chemicals (as of June 2008) or less than 1% of the 70,000 figure cited previously (U.S. EPA, 2008). This tremendous gap in information has been recognized and is being addressed by programs such as the Registration, Evaluation and Authorization of Chemicals (REACH) now being implemented in the European Union countries, the High Production Volume (HPV) Challenge underway in the U.S., as well as various industry sponsored initiatives (e.g., the Programme for Alternative Fluorocarbon Toxicity Testing). These regulatory programs will greatly increase the breadth of data available for chemicals present in the human environment and facilitate risk assessment. However, the rate at which such data can be acquired, evaluated, and used to generate toxicity criteria is limited. It is unlikely that these testing programs will remedy the substantial data gap in the near future. In addition, there are chemicals not covered by these regulations (e.g., process chemicals) which may nonetheless be involved in accidental exposures.

Along similar lines, standard exposure assessment methods may not be adequate for evaluating exposures that do not follow the standard environmental pathways, i.e., ingestion, inhalation or dermal contact with air, soil, or water. For example, assessments stemming from increased concerns about chemicals (e.g., nanomaterials) present in consumer products will require new exposure paradigms and supporting data. This expansion of risk assessment will also require the ability to think creatively and the willingness to accept a level of uncertainty in the results in order to develop timely answers to critical health risk questions. These needs may not be apparent to new students of risk assessment, among whom the ‘cookbook’ concept may seem to be the full story. For the benefit of such students, I give two case examples which illustrate how non-standard methods may be applied to answer pressing public health concerns.

2. Case 1 – Chemicals Lacking Toxicity Data

The first case example involves an accidental chemical release from an industrial facility into a surrounding residential area. The major chemical involved in the release was a reaction intermediate, 2-chloro-6-fluorophenol (CFP). Upwards of 100 individuals were potentially exposed to the chemical. Shortly after the release, emergency response agencies conducted sampling of both indoor and outdoor environments. Levels of CFP were detected in the indoor air of some residents’ homes, with high-end detected concentrations being approximately 0.2 $\mu g/m^3$. Biological monitoring data (urinary measurements of CFP metabolites) confirmed that residents had been exposed to the chemical. The question that had to be addressed in a fairly rapid manner was whether the presumed exposures represented a potential health risk. A quick review of standard toxicology databases and the medical literature indicated a lack of toxicological data on CFP. Material safety data sheets (MSDS) stated that the chemical was an irritant, particularly to the skin, eyes and mucous membranes but no dose or threshold for these effects was identified. One MSDS reported the LD50 in rodents to be in the range of 200–2,000 mg/kg. Anyone remotely familiar with chemical risk assessment will realize that these data are insufficient to evaluate potential human health risks. Thus, an alternative approach was required.

We began with a search for toxicity data on structurally-related chemicals. The use of structure–activity relationships (SAR) to estimate the properties of chemicals where such information is lacking from actual testing is a well established principle in the fields of toxicology, pharmacology and pharmaceutics (Wagner et al., 1995; McKinney et al., 2000; Perkins et al., 2003; Benigni and Bossa, 2006). The basic concept is that particular molecular constituents (e.g., hydroxyl groups, methyl groups, double bonds, ring structures, etc.) confer similar properties when present in otherwise different molecules. Certain of these chemical properties are related in predictable ways to biological effects (e.g., membrane solubility, lipid solubility, rate of metabolism, reaction with particular biological structures). Thus for example, oxygen (or hydroxyl) substitution may increase the potential reactivity with biological molecules but will also likely increase the rate of chemical elimination. The structure–activity approach may be highly quantitative (in the manner used to calculate numerical estimates for parameters such as octanol-water partitioning coefficients) but here a qualitative approach was judged to be more consistent with the nature of the toxicity available data.

The halophenols are a family of chemicals characterized by a phenol molecule covalently bound to one or more atoms of the halogen family: fluorine, chlorine, bromine or iodine. Although we did examine data on halobenzenes, we quickly decided that halophenols, and the dihalophenols in particular (i.e., phenols substituted with two molecules of fluorine, chlorine, iodine or bromine), would be most appropriate surrogates for CFP.

LD50 data for the halophenols are shown in Figure 1. As indicated in this figure, the data are most plentiful for the dichlorophenols (DCP). The data suggest that among the different halophenols, rodent LD50s are of the same order of magnitude (that is, within a factor of 2–10). Of the dihalophenols (for which toxicity data on the fluorine substituted members are unfortunately absent), 2.6-dichlorophenol (most analogous in structure to the compound of interest) has a relatively low LD50 of 2,100 mg/kg (NTP, 2002). The LD50 of 2.4-dichlorophenol (the most widely studied member of the group) has been reported to be 1,276 mg/kg (NTP, 1989), or about twice as acutely toxic, suggesting that 2,6 substitution may produce a compound of lesser toxicity. We also looked at the relationship of pKa and Kow between CFP and the halophenols. Both pKa (the acid dissociation constant) and Kow (the octanol-water

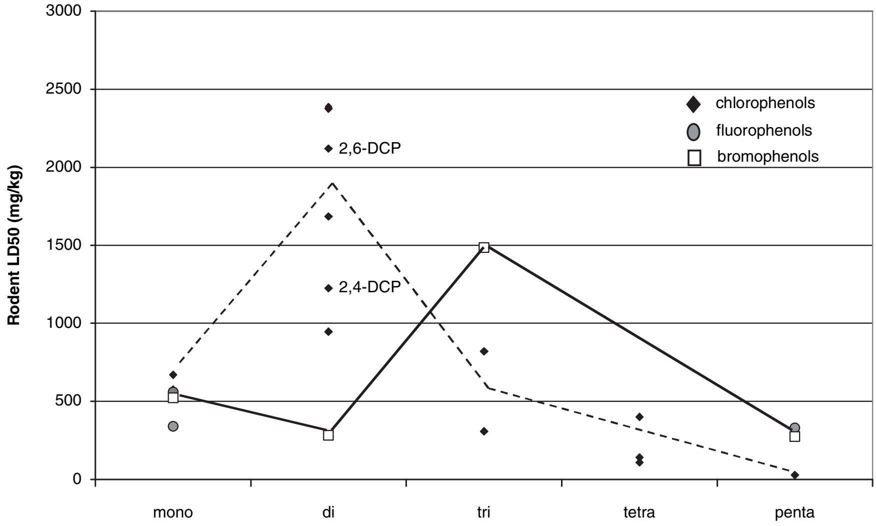

Figure 1. Rodent LD50 data for various halophenols. (Data taken from NTP 1989, 2002; WHO 1989.)

partitioning co(efficient) have been suggested as indicators of halophenol toxicity (Schultz, 1987). These evaluations (data not shown) also suggested that 2,6-dichlorophenol was the most appropriate surrogate compound and that use of 2,4-dichlorophenol as a surrogate would likely be conservative. We also considered a potentially more sensitive measure of chemical toxicity than the LD50, namely effects on mitochondrial oxygen consumption. A key toxic effect of halophenols is disruption of oxidative phosphoryllation (ATSDR, 1999). Izushi et al. (1988) evaluated the ability of different monohalophenols (phenol, fluorophenol, chlorophenol, bromophenol, iodophenol) to reduce mitochondrial oxygen consumption using isolated rat liver tissue (Figure 2). As shown in Figure 2, there was a clear relationship between the toxicity of the various phenols, with toxicity increasing in the order of fluoro < chloro < bromo < iodo. These data therefore also suggest that using dichlorophenols as toxicity surrogates for CFP is reasonable.

Toxicity data for 2,6-dichlorophenol (2,6-DCP) and 2,4-dichlorophenol (2,4-DCP) are available for evaluating the health effects of CFP. Due to a wide use in industrial applications, the toxicity data set for 2,4-DCP is more extensive than that for 2,6-DCP. The U.S. National Toxicology Program currently indicates there is no evidence that 2,4-DCP or 2,6-DCP are carcinogens. 2,6-DCP was negative in standard bacterial tests for mutagenicity (NTP, 2002). 2,4-DCP gave

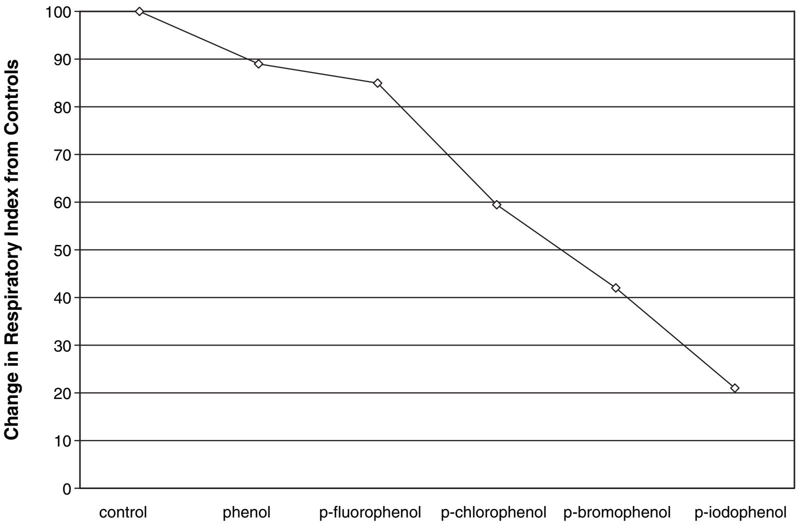

Figure 2. Effect of different halophenols on liver cell mitochondrial oxygen consumption. (Data taken from Izushi et al., 1988.)

equivocal results in bacterial mutagenicity tests but subsequent chronic bioassays in both mice and rats were negative (NTP, 1989). A number of toxicity criteria values have been established for 2,4-DCP. Health Canada (1987) has established an acceptable daily intake (ADI) of 100 μg/kg-day. The U.S. EPA has established an oral reference dose (RfD) of 3 μg/kg-day (U.S. EPA, 2008). Both values are intended to reflect levels of exposure that will be without adverse health risks. The substantial difference between the TDI and RfD results from the selection of different animal studies to derive a No Observed Adverse Effect Level (NOAEL); the Health Canada TDI was based on the mouse study of Kobayashi et al. (1972) whereas the U.S. EPA RfD was based on the later rat study of Exon and Koller (1985). In addition to these two oral exposure values, three U.S. states have established acceptable ambient air concentrations for 2,4-DCP. The values adopted by the states of Michigan, Texas and Arizona are 77, 53 and 1.6 μg/m^3, respectively (ATSDR, 1999). One Florida county (Pinellas) has also adopted an ambient air concentration for 2,4-DCP of 3 μg/m^3 (ATSDR, 1999).

To conduct a risk assessment one needs an estimate of exposure as well as a toxicity benchmark. For purposes of rapid risk assessment, we used the high end of the measured indoor air concentrations, 0.2 μg/m^3, as an indicator of indoor air levels of CFP. We assumed that an individual spends the entire day living within the home and breathing the indoor air (at a rate of 20 m^3 air/day, U.S. EPA, 1997a). Thus, the expected worst-case intake of CFP was 4 μg/day (0.2 μg/m^3 × 20 m^3/day). This value was then divided by an average human body weight of 70 kg, arriving at a dose estimate of 0.06 μg/kg-day.

Our indicator level of CFP measured in indoor air (0.2 μg/m^3) is one to two orders of magnitude below the acceptable ambient air levels for 2,4-DCP adopted by several state regulatory agencies. Considering possible internalized doses, the estimated dose of 0.06 μg/kg-day is approximately 50 times lower than the U.S. EPA RfD (3 μg/kg-day) and over 1,500 times lower than the Health Canada TDI (100 μg/kg-day) established for 2,4-DCP. The estimated exposure to 2-chloro-6-fluorophenol is also 500,000 times lower than the lowest effect level reported in animal studies of 2,4-DCP (30 mg/kg-day). Given these margins of safety, we concluded that adverse health effects would not be expected from this exposure. It should be noted that a subsequent assessment of exposures conducted by the Agency for Toxic Substances and Disease Registry followed a similar approach and reached similar conclusions (ATSDR, 2002).

The evaluation described above clearly engendered a level of uncertainty. Toxicity testing of CFP itself would of course have been desirable and use of such data in the risk assessment would have produced results of greater certainty. It is an unfortunate fact that additional data collection is often not possible in such situations due to time or financial constraints. Even an acute duration exposure study (i.e., 14-days) may require at least several months to plan, conduct and analyze the resulting data. In such situations it is not possible to wait until test data are available, although risk assessments may be revisited at later time points in order to refine the results. In the case described above, while the use of surrogate values for toxicity introduces some uncertainty, the margin of exposure is sufficiently large to give confidence in the conclusion that no adverse health effects would be expected.

3. Case 2 – Worker Exposure to Chemicals in Polyurethane Foams

We recently had the opportunity to determine whether worker exposures to methylenedianiline (MDA) and toluene diamine (TDA) during polyurethane foam manufacture could result in unacceptable health risks (described in detail in Lewandowski et al., 2005). Polyurethane foam is used in many applications including fabrication of residential furniture and seat cushions in automobiles and airplanes. During foam production, small amounts of MDA (4,4'-, 2,2'- and 2,4'- isomers) and TDA (2,4- and 2,6- isomers) are generated and may be present in newly manufactured foam products. Due to subsequent reactions within the foam, levels of these chemicals decrease rapidly and therefore pose little risk to consumers. However, workers handling newly synthesized foam may be exposed to these chemicals.

The polymerization process used to produce polyurethane foams is largely complete in less than 20 min. Starting materials are injected into a mold of the desired shape and then exothermic reactions combined with production of CO_2 causes the foam to expand and harden. After the formed part is removed from the mold it is trimmed, inspected and if defects are observed, hand repaired. Repaired parts are returned to the finished product line for curing and temporary storage, after which the parts are shipped off-site. Each step of the production process involves potential for human hand contact with the newly synthesized foam. For most tasks, contact with foam involves only the hands, although workers engaged in packaging and shipping parts may also contact foam via the forearms (if workers wear short sleeve or sleeveless shirts).

Toxicity data were available for these chemicals and lack of such data was therefore not an issue in this risk assessment. A cancer slope factor for 2,4-TDA was developed by the U.S. Food and Drug Administration based on a National Toxicology Program cancer bioassay of 2,4-TDA in rats and mice in 1979 (NTP, 1979; U.S. FDA, 1991). Long-term animal bioassays of 2,6-TDA have yielded negative results in terms of carcinogenicity but did yield an RfD of 0.2 mg/kg-day (NTP, 1980; U.S. EPA, 1997b). A cancer slope factor was not available for any of the MDA isomers and a margin of exposure approach was therefore used to assess carcinogenic risks. In this approach, the estimated intake (in mg/kg-day) was compared to the lowest dose shown to produce tumors in experimental animals; 18 mg/kg-day for 4,4’-MDA in a long term study of mice and rats (Weisburger et al., 1984). Non-cancer health risks for the MDA isomers were evaluated with an RfD (0.008 mg/kg-day) derived from study of Pludro et al. (1969).

3.1. EXPOSURE ASSESSMENT

The unusual aspect of this risk assessment involve estimation of worker exposures. Rather than dermal contact with a chemical present in some environmental medium (e.g., air, water) the exposure was to the pure chemical itself, located on the foam surface. Thus the standard exposure assumptions (which involve migration of chemicals from soil or water into the skin) were not relevant. Dermal contact with the foam was the only pathway considered in this evaluation. Inhalation of these chemicals was assumed to be relatively insignificant due to the low vapor pressures and, more importantly, the active exhaust ventilation located near employee workstations. Other potential pathways of worker exposure such as hand-to-mouth contact associated with smoking or eating were prevented by workplace policies and regulations.

Worker exposures to MDA and TDA were estimated by modifying the standard intake equation (U.S. EPA, 1989) as follows:

$$Intake\ (mg/kg\text{-}day) = \frac{FC \times \delta_f \times D \times SA \times TF \times ABS \times ET \times EF \times ED}{BW \times AT}$$

where:

FC = The concentration of MDA or TDA in the foam (mg/kg)
∂_f = The typical foam density (kg/m^3)
D = The depth of foam through which the chemical is accessible (cm)
SA = The skin surface area in contact with foam (cm^2)
TF = The fraction of chemical transferred from foam to hand (unitless)
ABS = The fraction of chemical absorbed through the skin (per h)
ET = The exposure time per day (h)
EF = The exposure frequency (day/year)
ED = The exposure duration (year)
BW = The body weight (kg)
AT = The averaging time (day)

Values used for the parameters in the intake equation and their basis are described in Tables 1 and 2. Values were obtained where possible from studies published in the scientific literature although in a number of cases (e.g., the values for d and TF) data were not available and the parameter values were based on scientific judgment. In these latter cases, we chose values which we believed to be highly conservative so as to err on the side of overprediction of risk.

In order to develop estimates of potential health risk, the intakes estimated using the equation shown above were combined with the toxicity values following standard risk assessment methodology (i.e., multiplication of the intake estimate and the cancer slope factors or dividing the RfD or tumorigenic dose by the intake estimate). The results of the risk assessment are shown in Table 3. The potential cancer risk attributable to 2,4-TDA exposure was 4.7 per 1,000,000 which is within the range typically considered acceptable in the U.S. for occupational exposures. The margin of exposure based on total MDA intake was approximately 60,000, meaning that the estimated worker dose of this chemical was over 60,000 times lower than the lowest dose reported to cause tumors in laboratory animals. The hazard quotient for long-term exposure to TDA (all isomers combined) was 0.04 and the hazard quotient for long-term exposure to MDA (all isomers combined) was 0.31. Thus, the combined hazard index was 0.35. Based on these results, we concluded that worker exposures to MDA and TDA during polyurethane foam manufacture did not pose a significant adverse health risk. Nonetheless, the results of this assessment were used to guide the design of a worker protection program which was aimed at reducing dermal exposures.

TABLE 1. Toxicological data available for surrogate phenols.

Compound	Effect	Dose (mg/kg)	Citation
2,4-DCP	LD50 (mouse, oral)	1,276	NTP, 1989
2,6-DCP	LD50 (mouse, oral)	2,198	NTP, 2002
2,4-DCP	Nasal irritation, inflammation	210	NTP, 1989
2,4-DCP	CNS depression	1,500	Kobayashi et al., 1972
2,4-DCP	Decreased body weight	5,200	NTP, 1989
2,4-DCP	Increased liver weight	30	Exon and Koller, 1985
2,4-DCP	Decreased litter size	30	Exon and Koller, 1985
2,4-DCP	Mutagenicity	Negative	WHO, 1989
2,6-DCP	Mutagenicity	Negative	NTP, 2002

TABLE 2. Parameters characterizing worker exposures to TDA and MDA in freshly synthesized polyurethane foam.

Variable	Description	Value	Basis
FC	MDA/TDA concentration in foam	Varies with stage of foam processing (mg/kg)	Manufacturer supplied analytical data
∂_f	Foam density	30 kg/m^3	Typical value (see Lewandowski et al., 2005 for details)
D	Depth of accessible chemical in foam	0.5 cm	Professional judgment
SA	Skin surface area exposed to foam	2,214 cm^2 – shippers 904 cm^2 – others	U.S. EPA, 1997a
TF	Transfer from foam to hand	0.5 (50%)	Professional judgment
ABS	Percent dermal absorption	TDA – 0.10 per h MDA – 0.28 per h	Highest reported values (see Lewandowski et al., 2005 for details)
ET	Exposure time	Weighted according to time spent on each processing task (h/day)	Based on facility site visits and observations
EF	Exposure frequency	260 day/year	Number of work days per year
ED	Exposure duration	7 year	Mean job tenure (U.S. EPA, 1997a)
BW	Body weight	70 kg	Mean U.S. male body weight (U.S. EPA, 1997a)
AT	Averaging time	Non-cancer effects: ED * 365 Cancer effects: 25,550 days	Averaging time differs for cancer and non-cancer endpoints (U.S. EPA, 1989)

TABLE 3. Results of risk assessment for worker exposures to MDA and TDA in newly synthesized polyurethane foams.

Chemical	Risk estimate for non-carcinogenic effects	Risk estimate for carcinogenic effects
MDA (all isomers)	0.30	85,000*
TDA (all isomers)	0.02	4.7×10^{-6}

*The carcinogenic risk for exposure to MDA was calculated as a Margin of Exposure (MOE) by comparing the estimated worker exposure level to the lowest tumorigenic dose in animal studies.

4. Conclusion

Risk assessors may be faced with situations where standard methodologies values are of little use. The two examples cited (one involving a chemical with inadequate toxicity data, the other involving a non-standard exposure pathway) demonstrate the need for risk assessors and regulators to be open to creative and flexible adaptations of standard methodology. While uncertainties were inherent in the approaches taken in both cases, the effect of the uncertainties on the final risk assessment results were believed to be small and acceptable given the need for conducting risk assessment as an input to risk management decisions. These two case examples illustrate some potential challenges in risk assessment but also demonstrate the value of flexibility and creativity for developing appropriate solutions.

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ASSESSMENT OF THE EFFECT POTENTIAL OF ENVIRONMENTAL CHEMICALS

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Abstract. The system employed for the modular total evaluation of chemicals according to their effect potential to human health (SCS – Substance-Characterization-System) classifies and evaluates their environmentally hygiene relevant properties by means of standardized coefficients. These SC-values enable potential threats to humans and the environment to be identified, quantified and repelled if necessary. The results of the SCS-method are then completed to tolerable concentrations if the SC-values predict a potential threat which is substance specific. This is achieved through a human toxicological assessment in the form of health guide values especially for drinking water. The system can thus basically be used to assess chemicals which have been released into the environment intentionally or unintentionally.

Keywords: hazard assessment system, human toxicity, eco toxicity, environmental chemicals, biochemical degradation, environment, substance characteristic, SCS-method

1. Introduction

In recent years the public has repeatedly been confronted with the fact, that environmentally relevant chemicals have been found in food and especially in drinking water. Some of these were found in concentrations which surpassed

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the maximum admissible value (Becker et al., 2007; Dieter et al., 1996; Grohmann and Winter, 1993; Mulisch et al., 2008; Rhein et al., 2002; ULIDAT, 2008). The following examples have been cited:

- Acetaldehyde found in beer and wine.
  Reason: ethanol oxidates if not treated or stored appropriately.
- Melanin found in milk sweets.
  Reason: adulterated milk.
- Benzene found in lemonades and fruit juices.
  Reason: benzoic acid which is used as a preservative reacts with vitamin C.
- Insecticides, fungicides and herbicides found in drinking water and other foods.
  Reason: prohibitions ignored or inappropriate usage.
- Drinking water contaminated with lead.
  Reason: lead water supply pipes.
- Pharmaceutical products found in drinking water.
  Reason: some medications in use today are so resistant that they neither degrade in the human body, in sewage plants, nor in the environment.
- Nitrate found in vegetables, especially in lettuce.
  Reason: mineral fertilizers used inappropriately.

It is proven that we are exposed to thousands of chemicals on a daily basis. This can occur through food, drinking water, air or through direct skin contact. This exposure can either be:

- Intentional, for example through:
  - Food additives, such as food colorings, preservatives, antioxidants, etc.
  - Agents used in the textile industry, such as tensides, softeners, etc.
  - Pesticides
- Unintentional, for example through:
  - Industrial, military waste
  - Degradation products of the chemical industry
  - Fumes emitted by vehicles, heating systems, etc.

2. The Substance Characterization-System (SCS) Employed for the Modular Total Evaluation of the Potential Effects of Chemicals

The legislator passes laws which clearly define maximum admissible values and test values to protect human health. Such laws can be found in German regulations regarding the soil and drinking water (Trinkwasserverordnung, 2001; Konietzka und Dieter, 1998). Thus a regulation dating back to May 28th 2001 states that drinking water must not contain chemicals in concentrations which could be potentially harmful to human health. Values which require measures to be taken correspond to the defined maximum admissible values. Such threshold values are predefined maximum admissible concentrations of chemicals found in food, drinking water and the environment. The choice of these concentrations is rarely based on health considerations alone. They can be chosen in such a way as to prevent illnesses, protect the water distribution system or to reflect the current state of technology. The choice can also have ecological motives (Allgemeine Verwaltungsvorschrift, 2005) or be explained by the technology of the plant. Thus these values can often be misinterpreted and be considered to mark the borderline between a healthy and health hazardous environment.

A purely health orientated standardized procedure is necessary in order to be able to assess, prioritize and avert actual potential threats to humans. A comprehensible, practical but nevertheless strictly scientifically based system will be presented which primarily focuses on toxicological relevance. This Substance-Characterization-System (SC-System or SCS) enables the calculation of coefficients by means of substance specific properties (= substance characteristics) in order to assess a chemical's potential dangerousness. The substance specific characteristics regarding biochemical degradability (SC_{BIO}), mobility in the environment (SC_{MOB}), human toxicity (SC_{TOX}) and aqua toxicity (SC_{AQU}) and the resulting connections are determined via individual standardized evaluation grids (SC-grids). (see Table 1).

Apart from the SC_{BIO}-grid, the evaluation of the toxicological relevance SC_{TOR} of a chemical also contains the evaluation of human toxicity (SC_{TOX}-grid) and aqua toxicity (SC- grid) by taking into consideration data of chronic and subchronic toxicity, reproductive toxicity, toxicological kinetics, genetic toxicity, carcinogenic properties and other environmentally relevant toxicological key values. The results of the dangerousness of individual chemicals or are listed in the form dimensionless key values SC_{TOR} which can take values from 2 to 6. Table 2 shows several examples.

3. The Health Guide Value (LW)

Another important result of the SC-System is the integration of the health guide value (LW) which is based upon human toxicity. This value is not intended to replace a potential threshold value, but is intended to be a reference to human health or to human threats if exceeded (see Table 1). Thus times of exposure with little or no risks can be extrapolated, from which time structured test values and measure values can be calculated. The health guide values are related to exposures to chemicals in drinking water, they can also be applied to other foods or to exposures in the environment, if one is able to judge the extent of the exposure to a certain environmental chemical. This respects the wishes of consumers, traders and authorities which all demand improved quality management and compulsory, scientifically backed maximum admissible values.

TABLE 1. Description of the substance characteristic system (SCS).

Obligatory SCS parameters		Hazard identification	
Substance evaluation		Exposure	Health guide values (LW)
Substance characteristics	Range of values	⇨	
SC_{TOX}	1.0–4.0		LW
SC_{BIO}	1.0–2.0	⇨	LW_{KE}
$SC_{TOX} + SC_{BIO} = SC_{TOR}$	2.0–6.0		LW_{SK}
$SC_{LÖS}$	1.0–2.0		HSO
SC_{ADS}	1.0–2.0	⇨	
SC_{MOB}	2.0–4.0		
SC_{AQU}	1.0–2.0		HZK

Legend:

Substance characteristics SC:

TOX = Human toxicity
TOR = Relevance for environmental toxicity
ADS = Adsorbability
AQU = Aqua toxicity
BIO = Biochemical degradation
LÖS = Water solubility
MOB = Mobility

Hazard identification:

LW = Health guide value
LW_{KE} = Time-dependent exposure guide value
LW_{SK} = Key value for infants and small children with short exposure
HSO = Hygienic-sensorial max. value
HZK = Max. admissible concentration (aqua toxicity)

To calculate the health key value for lifelong exposure (LW), 10% (to 50%) of the TDI-value are multiplied with the weight of 70 kg and distributed over 2 L of drinking water.

$$LW = \frac{TDI \cdot 70\ \text{kg}}{10 \cdot 2\ \text{l}}$$

The TDI (*tolerable daily intake*) represents the daily dose in mg/kg/day which is admissible lifelong. Information on the calculation of the LW for short and long exposures to carcinogen substances can be found in the literature (Dieter und Hänseling, 2003; UBA, 2003).

TABLE 2. Examples of the dangerousness of chemicals shown by means of the SC-system.

Environmental chemical	Toxicological relevance of SCS as SC_{TOR}	Statement	
		Dangerousness	Necessity to act
Glykole	2.2	Low	Unlikely
Toluene	3.3	Medium	Low
2,4-Dimethyltoluene	4.5	High	Probable
2,4,6-Trinitrotoluene	6.0	Very high	Absolutely essential

4. The Maximum Admissible Value (HZK) of Chemicals in the Environment

The SCS allows potential dangers of chemicals with high SC_{AQU} values to be quantified via a aqua toxicological maximum admissible concentration (HZK).

$$\text{HZK} = \frac{\text{NOEC bzw. LOEC} \cdot \cos\alpha}{\text{EF}_1 \cdot \text{EF}_2 \cdot \text{EF}_3 \cdot \text{EF}_4} \ \text{[mg/l]}$$

where,

NOEC	Highest concentration without visible effects, test duration specified
LOEC	Lowest concentration which causes visible damages, such as respiratory problems and loss of balance
α	Slope of the function in the 10log-System (cos a = max.0.3)
EF_1	Extrapolation factor to estimate the safe NOEC or the marginal concentration of the deepest, unsafe
LOEC	In this case $EF_1 = 10$. If NOEC has been measured, $EF_1 = 1$.
EF_2	Extrapolation factor dependent on the biochemical degradability which is an indicator for the aqua toxicological hazard of a chemical. EF_2 = SCBIO
EF_3	Extrapolation factor to assess the quality of the documented values. $EF_3 = 1$ if assessment is safe and sufficient. $EF_3 = \sqrt{3}$ if two or more contradicting assessments exist; $EF_3 = 3$ if only one data source or assessment exists
EF_4	$EF_4 = 10$. Extrapolation factor only for intensively used waters, such as for fishing; for natural waters $EF_4 = 1$.

If the HZK is not exceeded, damages to water organisms can be ruled out. If the HZK lies under the health key value, all conditions to guarantee the health safety of drinking water are met.

5. Results

Until now approx. 140 chemicals have been assessed in studies according to the SC-System. (Mulisch et al., 2001, 2008). Table 3 shows some examples of frequent chemicals (in decreasing order according to their dangerousness). SC-values without brackets are based upon sufficient data. Values in brackets are only preliminary as some important data are missing. However, preliminary values with missing data can be taken into consideration if they are based upon sufficient experience. Half lives $t_{1/2}$ can be deducted from the SC_{BIO}-values under natural conditions. Thus a chemical with SC_{BIO} 1.8 can be expected to have a half life of several years.

Further details can be found in the WaBoLu-booklets 03/08 of the Federal Environmental Agency (Mulisch et al., 2008). The authors are willing to assess chemicals in respect to the SC-values, health key values and the resulting time structured values.

TABLE 3. Assessment of chemicals by the means of SC_{TOX} and SC_{BIO} and the resulting toxicological relevance SC_{TOR}.

No.	Chemical composition	Name of the environmental chemical	SC_{TOX}	SC_{BIO}	SC_{TOR}
1	Na_2CO_3	Soda	1.0	1.0	2.0
2	$C_{12}H_{25} \cdot C_6H_4 \cdot SO_3Na$	Dodecylbenzolsulfonate (ABS, tenside)	(1.5)	1.3	(2.8)
3	CH_3OH	Methanole	2.0	1.0	3.0
4	C_nH_m	Gasoline	(2.0)	1.8	(3.8)
5	C_6H_5OH	Phenole	3.0	1.0	4.0
6	C_6Cl_5OH	Pentachlorophenole	3.0	2.0	5.0
7	C_6H_6	Benzole	4.0	1.5	5.5
8	$C_6H_2 \cdot Cl_3 \cdot O \cdot CH_2 \cdot COOH$	Trichlorophenoxy-acetic-acid (Herbizid)	(4.0)	1.8	(5.8)
9	$C_6H_{0\text{-}4}Cl_{1\text{-}5} \cdot C_6H_{0\text{-}4}Cl_{1\text{-}5}$	Polychlorinated biphenyls (PCBs)	4.0	2.0	6.0

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MODELING CHEMICAL EXPOSURES IN RISK ASSESSMENT

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Abstract. Risk assessment is increasingly concerned with assessing risks from environmental exposure pathways beyond those typically considered, i.e., direct ingestion, inhalation or dermal exposure to chemicals in air, water, and soil. A number of models have been developed to facilitate analysis of these more complex exposure situations. Such models also enhance our ability to assess both aggregate and cumulative exposures. Three different modeling approaches are described which address some of these issues; the U.S. EPA's IEUBK model for lead, the multipathway health risk assessment (MPHRA) methodology developed for assessing risks of incinerators and waste combustors, and the U.S. EPA's Stochastic Human Exposure and Dose Simulation (SHEDS) model.

Keywords: exposure models, cumulative exposure, aggregate exposure

1. Introduction

Risk assessors frequently use the terms aggregate and cumulative exposure. Although the terms may seem interchangeable, they in fact have distinct meanings. Aggregate exposure refers to exposures to a *single* chemical via multiple routes or pathways; cumulative exposure refers to exposures to *multiple* chemicals via multiple routes or pathways (U.S. EPA, 2008). Cumulative exposure is particularly important when chemicals have common or inter-related toxicological effects. Risk assessors may also distinguish between direct exposures, those that involve contact with the primary contaminated media (soil, water, air), and indirect exposures; those that involve contact with environmental media that have been contaminated by pollutants moving out of their initial environmental sink (e.g., foodstuffs contaminated by chemicals in air or soil, indoor air contaminated by volatile organic compounds in groundwater beneath a building, etc.)

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Exposure assessment involves estimating the transfer of a chemical substance from an environmental medium into the human body. For environmental pollutants, this typically involves direct exposure *via* ingestion, inhalation or transdermal absorption of chemicals in soil, air, or water. In a typical environmental risk assessment, one estimates exposures to each chemical by exposure pathway, adds the exposure to each chemical (i.e., the aggregate exposure), and compares the resulting exposure value to some toxicity criterion (e.g., a reference dose). The ratios of the individual chemical exposures to their respective toxicity criteria, often called hazard quotients, are then added (i.e., cumulative exposure). With the implicit assumption that health risks are additive, the goal is to have the sum of the hazard quotients be below 1.0, meaning that exposures do not present a health concern (U.S. EPA, 1989a).

In addition to the common exposures to air, soil and water, exposures may result from other activities such as pesticide application, use of chemical containing consumer products, introduction of chemicals into the home from clothes worn in the workplace, or consumption of foods that have been grown or processed in polluted areas. Increasingly, risk assessment involves evaluation of these less common exposure pathways through the use of more sophisticated exposure modeling. In the following sections, I present three examples of models that have been used to evaluate aggregate and/or cumulative exposures.

2. The Integrated Exposure Uptake Biokinetic (IEUBK) Model for Lead

One early example of a risk assessment model developed to assess the aggregate risks of environmental pollutant exposure is the U.S. EPA's Integrated Exposure Uptake Biokinetic (IEUBK) model for lead (U.S. EPA, 1989b, 2007). This model estimates blood lead concentrations in children 0–6 years of age based on the concentrations of lead in different environmental media where the children live. The model has also been used to "backcalculate" lead cleanup levels; essentially determining the level of lead in a given environmental medium (typically soil or dust) which is necessary, given the expected lead concentrations in other media, to achieve acceptable blood lead levels in resident children. The model runs on a regular PC computer and requires no particular computer programming skills. Note that the model is only applicable to children, other models have been developed to address adult exposures (e.g., Pounds and Leggett, 1998; Bowers and Cohen, 1998).

First developed in the late 1980s, the model has subsequently been revised and updated over time and been the subject of much review and discussion (U.S. EPA, 1989b; Lewandowski and Forslund, 1994; LaKind, 1998; Griffin et al., 1999). The model addresses aggregate exposure from the major environmental media of concern for lead toxicity (i.e., food, drinking water, air, soil, dust, ingested paint chips). The model combines site-specific lead concentration data (e.g. measurements of lead in water, soil, dust, paint, and air) with standard exposure values (e.g., the rate at which a typical child breathes, consumes water, or ingests soil or dust) to estimate lead intake. The model contains default values for all environmental media concentrations although the user is strongly encouraged to use site-specific data to obtain the most relevant results. For exposures to lead in food, standard food consumption rates and U.S. FDA data on the historical lead content in food are used. The model also accounts for the transfer of lead across the placenta from the mother during the fetal period, allowing the user to either include site-specific data (e.g., from a blood lead monitoring program) or to rely on a national default value.

Once the lead exposure from each exposure pathway is estimated, the model calculates the internal dose and resulting concentration of lead in blood using absorption factors and tissue distribution ratios, rates of lead storage and elimination (via urine, feces, skin, hair, and nails), and accounting for the increasing size of the growing child's tissues. Lead absorption and elimination are both age- and media-specific and are predicted based on a combination of human and animal data. The primary outputs of the model are the predicted blood lead level and the percentage of children in a theoretical population with the modeled exposures that would have blood lead levels above a level of health concern (typically 10 μg/dL). The latter estimate is obtained by applying a geometric standard deviation (GSD) to the predicted blood lead value. The GSD value is therefore intended to account for interindividual variability in both lead exposure and lead kinetics.

It should be noted that the IEUBK model will not reliably predict blood lead levels based on exposure for single individuals. Because the model relies on average values for many of its inputs (e.g., for soil ingestion, for lead biokinetics) it can only be expected to yield accurate predictions on a population level. The IEUBK model was validated using blood lead and environmental lead data obtained at several large sites of lead pollution in the U.S. (Zaragoza and Hogan, 1998; Hogan et al., 1998). The IEUBK model has been used by the U.S. EPA and various U.S. state agencies to set the national ambient air quality standard for lead and to establish cleanup criteria at numerous sites of environmental lead contamination (U.S. EPA, 1994a).

3. Multipathway Health Risk Assessment (MPHRA)

The example given above pertains to only one specific chemical (and thus only addresses aggregate exposures) and a narrowly defined receptor population (i.e., children 0–6 years of age). Another methodology that includes the potential for evaluation of cumulative risks has been developed to assess the risks posed by incinerators and other chemical combustion facilities (U.S. EPA, 1994b, 1998, 2004, 2005a, b). The impetus for this risk assessment approach was the recognition that such facilities release dioxin and other environmentally persistent chemicals into the environment. The Multipathway Health Risk Assessment (MPHRA) methodology involves using a series of fugacity-based equations to estimate chemical concentration in different environmental media. Fugacity refers to the tendency of chemicals to partition between pairs of media having dissimilar properties such as air:water or fat:water. The methodology is particularly suitable to estimating risks for lipid soluble chemicals such as dioxins, dibenzofurans and polychlorinated biphenyls (PCBs), which accumulate in biological tissues and food chains. The MPHRA equations can be easily implemented in commercial spreadsheet programs. Typical exposure pathways considered in the MPHRA approach include the following:

- Direct exposure to contaminated soil, air, groundwater, and surface water
- Exposure via ingestion of contaminated plant material (foliage, roots)
- Exposure via ingestion of contaminated meat, eggs and dairy products
- Exposure via ingestion of contaminated aquatic life, and
- Exposure via breast milk

Typical receptors considered include residents with home gardens (who thus exposure to homegrown produce), farmers, consumers of local fish and, where applicable, subsistence populations who may have higher intakes of locally produced foods. Exposures are usually assessed for adults, children and infants (the last being highly dependent on ingestion of breast milk and cow's milk). The novel element of the MPHRA approach is the use of alternative equations to conduct a detailed exposure assessment; the toxicity assessment and risk characterization stages are handled in the manner of a standard risk assessment (see U.S. EPA, 1989a).

The overall scheme for the MPHRA risk assessment is shown in Figure 1. From the point of release, the pollutants of concern are followed through the different environmental media (e.g., soil, water, air, plant tissue, animal tissue) up to the point of human contact. The extent of the environmental release is usually determined by monitoring (e.g., stack emissions) although modeling (e.g., to simulate different operating conditions) is also possible. Modeling of chemical fate and transport after the initial release is generally performed with standardized models.[1] The results of the fate and transport models then serve as inputs to the fugacity-based equations.

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[1] For example, models used to estimate fate and transport in air include ISC3 (U.S. EPA, 1995a) and Calpuff (U.S. EPA, 1995b). Three publicly available models commonly used to predict

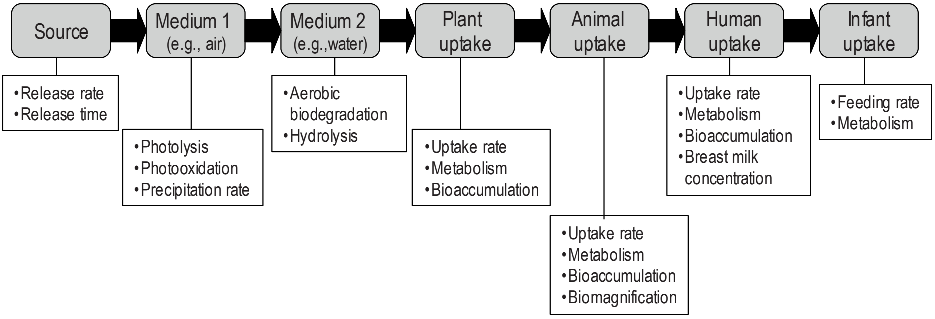

Figure 1. Conceptual model for the multipathway health risk assessment approach. The contaminants of interest are followed from the point of release to the point of human exposure, through various environmental media. At each step in the process, mathematical models are used to predict chemical transfer, degradation, and accumulation. Examples of potentially relevant transfer, degradation or accumulation processes for each stage of the model are indicated in the boxes below each stage.

The equations used to predict uptake into biological media can be fairly simple, as illustrated in this example for calculating fish tissue concentration:

$$C_{fish} = C_{dw} \bullet BCF_{fish} \qquad \text{(Equation 5-48 in U.S. EPA, 2005a)}$$

where:

C_{fish}	Concentration of compound in fish tissue (mg/kg)
C_{dw}	Dissolved phase water concentration (mg/L)
BCF_{fish}	Bioconcentration factor for chemical in fish (L/kg)

Other equations may be complex, such as the following, used to estimate the chemical concentrations in beef:

$$A_{beef} = (\Sigma(F_i \bullet Q_{pi} \bullet P_i) + Q_s \bullet C_s \bullet B_s) \bullet Ba_{beef} \bullet MF \quad \text{(Equation 5-22 in U.S. EPA, 2005a)}$$

where:

A_{beef}	Concentration of chemical in beef (mg/kg)
F_i	Fraction of plant type i grown on soil ingested by the animal (unitless)
Q_{pi}	Quantity of plant type i eaten by animal per day (kg/day)
P_i	Concentration of chemical in plant type I (mg/kg)
Q_s	Quantity of soil eaten by the animal each day (kg/day)

chemical fate and transport in groundwater include MODFLOW (U.S. EPA, 1993), MT3D (U.S. EPA, 1992) and 3DFATMIC (U.S, EPA, 1997). A model for estimating chemical fate in sediment is the CEMC Sediment model (www.trentu.ca/academic/aminss/envmodel/models/Sedt2.html). The choice of specific models should be based on knowledge of site-specific conditions.

C_s	Average soil concentration over exposure duration (mg/kg)
B_s	Soil bioavailability factor (unitless)
Ba_{beef}	Chemical biotransfer factor for beef (day/kg tissue)
MF	Chemical metabolism factor (unitless)

Note that the results from a series of separate plant uptake equations are required as inputs to the above example to estimate chemical transfer from plant tissue to beef. Key parameters in these equations (i.e., the various bioconcentration or biotransfer factors) are estimated from octanol-water partition coefficients and empirically observed relationships (Birak et al., 2001; RTI, 2005). Thus, for example:

$$Ba_{beef} = 10^{\log(Ba_{fat})} \bullet 0.19 \quad \text{(Equation A-2-23 in U.S. EPA, 2005b)}$$

$$\log Ba_{fat} = -0.099\ (\log K_{ow})2 + 1.07\ K_{ow} - 3.56 \quad \text{(Equation A-2-21 in U.S. EPA, 2005b)}$$

where:

Ba_{fat}	Biotransfer factor (mg/kg fat)
K_{ow}	Octanol-water partition coefficient

Estimation of bioconcentration factors from K_{OW} values does introduce uncertainty into the results which should be discussed in the conclusions of the risk assessment. In developing the bioconcentration–K_{OW} relationship, U.S. EPA scientists did examine empirical biotransfer data for a large number of organic chemicals (log K_{OW} values ranging from approximately –1 to 8). They found a consistent relationship between K_{OW} and biotransfer that was described by a polynomial of the form $y = ax^2 + bx + c$. The fit of the data was greatly enhanced by adjusting K_{OW} values for organics that are either highly metabolized or ionizable (RTI, 2005).

The MPHRA approach represents an easy-to-implement method for assessing cumulative (and aggregate) risks from exposure to environmental chemicals. It is well suited for screening level risk assessments where worst-case assumptions can be employed in place of measurement data (where such data are lacking) or as a precursor to using sophisticated environmental fate and transport models. If the results of the worst-case assessment suggest exposures may be of concern, the risk assessment can be revisited with more rigorous data to obtain more accurate risk estimates.

4. Stochastic Human Exposure and Dose Simulation (SHEDS) model

As suggested by its name, the Stochastic Human Exposure and Dose Simulation (SHEDS) model is designed to yield probabilistic estimates of human exposure. The model uses a Monte Carlo approach, in which values for exposure variables are drawn from data distributions repeatedly in a large number of iterations, yielding a distribution of output predictions. Development of this model began at U.S. EPA's office of Research and Development in 1998 and has continued in the form of improved and updated versions to the present day.

The SHEDS model addresses exposures resulting from inhaling contaminated air, touching contaminated surfaces, and ingesting chemicals from the diet and hand-to-mouth contact. Using a series of database files containing information on the frequency and range of human activity patterns (e.g., Consolidated Human Activity Database, CHAD) and physiological variables (e.g., body weight, inhalation rate), the SHEDS model generates daily exposure estimates (i.e., dose-time profiles) for a large population of theoretical individuals. The model then uses that set of individual estimates to predict the range of human exposures on a population level. Through use of the Monte Carlo approach, the SHEDS model can also generate a sensitivity analysis, identifying the most critical input variables for the model. It will also describe the uncertainty in the final estimates based on the combined uncertainties of the input variables. The model's exposure estimates can then be used in a simple pharmacokinetic model (based on 1st order kinetics with chemical-specific data as inputs) to predict internal blood concentrations or excretion rates. These values can then in turn be compared to chemical-specific biomarkers of toxicity (Figure 2).

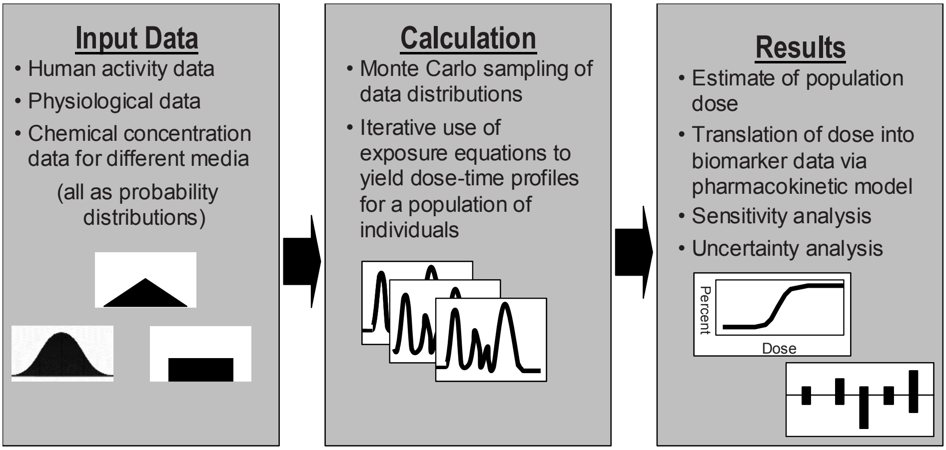

Figure 2. Conceptual approach for U.S. EPA's Stochastic Human Exposure and Dose Simulation (SHEDS) model. (Adapted from Watkins, 2004.)

SHEDS is currently coded in the SAS programming language and thus the user must also have a licensed copy of the basic SAS statistical package in order to run the SHEDS model. A key advantage of the SHEDS model is its ability to estimate potential exposures over time, taking into account seasonal changes in activity and decreases in chemical concentration (e.g., from one time application of pesticides). The model therefore has the ability to generate dose estimates for different time frames of interest (e.g., peak dose, monthly dose, lifetime dose).

The SHEDS model has been used to evaluate different pesticide exposure situations. For example, scientists at U.S. EPA have published an evaluation of children's exposure to the insecticide chlorpyrifos, looking at uptake and internal dose from both broadcast and crack and crevice treatment (Zartarian et al., 2000). The model was used to predict blood and urinary chlorpyrifos metabolite concentrations in children of different age groups (0–4 years of age and 5–9 years of age), in response to two different forms of application (broadcast and crack/crevice), and at three timeframes post-application (<1 day, 1–7 days, and 8–30 days). The authors reported that chlorpyrifos metabolite levels in blood and urine were 1–2 orders of magnitude lower with crack and crevice application than with broadcast application. Metabolite concentrations were also roughly eight times lower in the time period 8–30 days post-application as compared to the 1–7 day period (Zartarian et al., 2000), thus suggesting a fairly rapid decreased in exposure-related risk with time. More recently, the model has been used to evaluate children's exposures to chromated copper arsenate (CCA) from treated wood structures such as play sets (Zartarian et al., 2006; Xue et al., 2006).

The current version of the SHEDS model (SHEDS-multimedia v3) is currently limited in the number of exposure pathways that can be evaluated and is thus not entirely capable of evaluating aggregate exposures. U.S. EPA has indicated that the next version of the model (now under development) will permit probabilistic assessment of both aggregate and cumulative risks (i.e., risks to multiple chemicals via multiple direct and indirect pathways), providing substantial improvement over deterministic methods such as the MPHRA methodology. The SHEDS model is expected to become a significant tool for establishing environmental health regulation in the U.S. and may be a useful evaluation tool in other jurisdictions as well.

5. Conclusions

The three models described above demonstrate the increasing breadth and sophistication of efforts used to assess the potential human health effects of environmental exposures. The field of risk assessment has evolved considerably from the early 1980s when simple algebraic equations characterized the state of the art in exposure assessment modeling. As the needs of risk assessment have expanded (*e.g.*, addressing potential interactive effects of cumulative exposures, considering impacts of exposure at different life stages, linking exposure patterns with biomarker data, evaluating highly variable or discontinuous exposures, *etc.*), so too has the need for exposure modeling tools of appropriate scope and realism.

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COMPLEX CHARACTERIZATION OF POLLUTED SAMPLES

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Abstract. Environmental risk assessment (ERA) is a complex process that requires specific data to be processed, in order to give relevant and certain information about the possible risks that could affect the status of human and ecological health. As part of the ERA activity, exposure assessment results are relaying on monitoring data as well as on models that are developed based on quite sophisticated equations, requiring a lot of information. Environmental monitoring is, therefore, a complex surveillance process of which purpose is to deliver the most relevant information on the accumulation, persistence or dispersion in space and time of the pollutants in the environmental compartments (air, water, soil and biota), considering all their specific sub-systems: aerosols, suspensions, groundwater, surface water, soils, sediments, microorganisms, plants, animals, humans. The actual paper is aiming to give a basic and simple description of the environmental monitoring process, with emphasis on the analytical stages of the pollutants determination: principles of sampling and chemical analytical methods and techniques that are used for the complex characterization of polluted samples.

Keywords: risk assessment, environmental monitoring, sampling, analytical methods, analytical techniques

1. Introduction in Environmental Risk Assessment

According to the American Chemical Society (ACS, 1998), environmental risk analysis comprises three main activities: (1) environmental risk management; (2) *environmental risk assessment*; (3) environmental risk communication.

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Environmental risk assessment (ERA) is a complex activity consisting in the examination of risks resulting from natural events or industrial activities (processes, technology, products), that may affect or threat the entire ecosystems, animals and people. Two main components of ERA were identified: *health risk assessment* (addressed to human health) and *ecological risk assessment* (addressed to the environmental media and organisms). ERA is a scientific activity involving a critical review of available data aiming to identify and possibly quantify the risks associated with a potential threat. ERA is a formal mathematical tool used to evaluate potential hazards caused by pollutant emissions, affecting the human health and the environment (Calow, 1998; Betianu and Gavrilescu, 2006), based on some or all of the following elements: (1) hazard identification; (2) effects assessment; (3) *exposure assessment*; (4) risk characterization.

Exposure assessment consists in emissions determination, pathways and rates of movement of a substance and its transformation or degradation in order to estimate the concentrations/doses to which *human populations or environmental compartments* are or may be exposed. Exposure estimation involves combining predicted concentrations for target chemicals (with certain assumptions about the environmental fate of these chemicals) with the activity patterns of the receptors. Subsequently, the results of the exposure assessment include toxicity and epidemiological information to provide a quantitative estimation of risk.

Humans may be exposed to pollutants directly in their workplaces (occupational exposure), and/or indirectly via the environment. The human health risk assessment phase of exposure assessment gives the estimation of the rates of which chemicals are receipted. Because most potential receptors can be exposed to chemicals from a variety of sources and/or in different environmental media, an evaluation of the relative contributions of each medium and/or source to total pollutant intake could be critical in a multipathway exposure analysis (Betianu and Gavrilescu, 2006; Ilie and Gavrilescu, 2006). Ecosystems may be exposed to chemical substances during all stages of their lifecycle, from production to disposal or recovery. The objective of the ecological exposure assessment is to estimate the concentration to which environmental compartments are or may be exposed. The process for the environmental risk assessment of a substance is based on the comparison of the concentration in the environmental compartment (predicted environment concentration, PEC) with a concentration below which unacceptable effects on organisms will most likely not occur (predicted no effect concentration, PNEC). Therefore the aim of exposure assessment for the environment is the evaluation of PEC. (Sutter II and Sutter, 2006).

The exposure assessment is based on representative *monitoring data* and/or *on model calculations*. Therefore, for a typical exposure analysis of the environmental contamination, the following steps must be followed (Gavrilescu, 2008):

(1) *environmental monitoring* (determination of the concentrations of the xenobiotics of concern in each medium to which potential receptors are or may be exposed; (2); *fate and exposure models* (intakes estimation of the chemicals of concern).

Measured exposure data may be available for existing substances, during a known period and place, but are unavailable for new substances, different times or places. The latter may be obtained from industry monitoring programs (particularly for occupational exposure), or integrated monitoring programs. For ERA purposes, the types of environmental monitoring can be classified as follows:

- *Biological monitoring* – allows measurement of exposure and accurate assessment of likely health outcomes; it involves analysing human biological samples (blood, urine, hair, breast milk) for the presence of target chemicals.
- *Environmental monitoring* – allows measurement of exposure and accurate assessment of likely ecological outcomes; it involves analysing environmental samples (air, soils, water, biota) for the presence of target chemicals.

When starting an environmental risk assessment process there are two possible ways to approach it (top-down or bottom-up): one can follow the ERA development stages (top-down), or data pathway, from the data providers to the environmental risk assessors (bottom-up), as suggested in Figure 1. Any procedure you may follow, valid and reliable data are compulsory, and the procedure to acquire these data is the environmental monitoring.

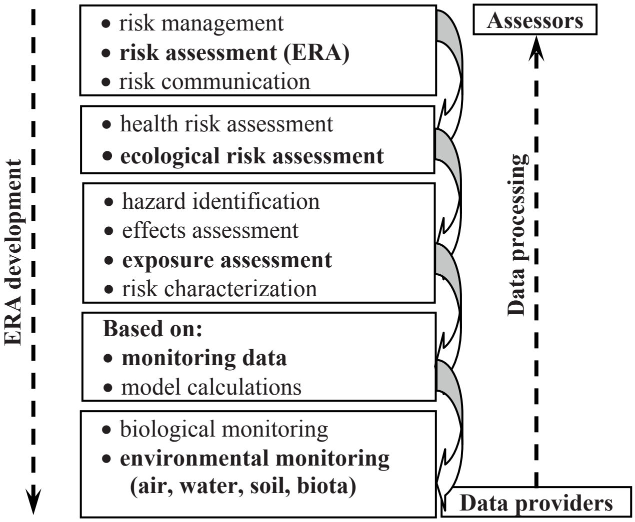

Figure 1. Environmental risk assessment approach.

Following the introductory approach, from ERA to environmental monitoring data, the actual paper is aiming to give a basic and simple description of the environmental monitoring process, not focused on the integrated monitoring system, but on the analytical stages of the complex characterization of polluted samples, especially on the principles of sampling and chemical analytical methods.

2. Environmental Monitoring

Evaluation of the status of the natural environment represents the basic element of a monitoring system. The evaluation steps include selection of the environmental characteristics and indicators, their direct measuring, as well as the data evaluation. For each potentially exposed environmental compartment, the exposure concentrations should be evaluated by environmental monitoring activities.

Environmental monitoring is a complex surveillance process aiming to deliver the most relevant information on the accumulation, persistence or dispersion of the pollutants in environmental compartments (air, water, soil and biota), considering all their specific sub-systems: aerosols, suspensions, groundwater, surface water, soils, sediments, micro-organisms, plants, animals, humans. A general description of the environmental monitoring stages is given in Figure 2, including the most important *processes* and their intermediate *results*. When an environmental undesirable event occurs, the problem should be carefully defined, in order to allow planning the required procedures, formulating the objectives and their related actions (Duta and Colbeck, 2004). The analytical process is following for the measurements and data acquisition. These data are further processed and evaluated, as evolutions in space or time of the pollutants concentration. In the specialised laboratories, all these operations are subject of quality assurance (QA) and quality control (QC).

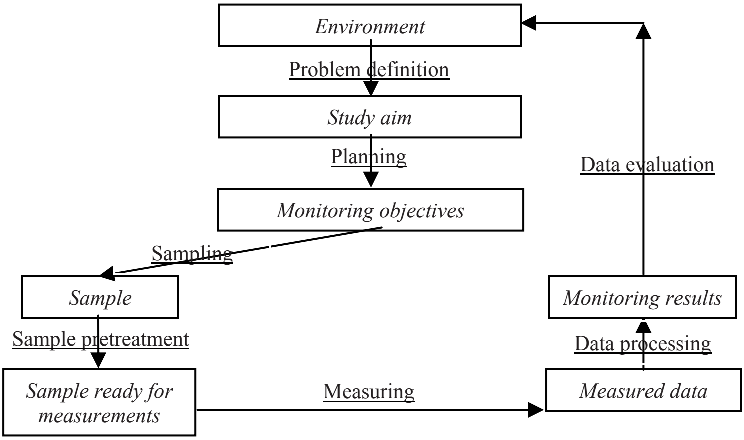

Figure 2. Block scheme of the analytical process, part of the environmental monitoring.

2.1. ENVIRONMENTAL MONITORING TYPES

The monitoring can be conducted having two main different targets, affected by the pollution and/or other influencing natural or anthropogenic factors:

- *Environmental monitoring* – surveying the environment components (Figure 2)
- *Biological monitoring* – surveying the health status of the plants and animals

Specialists in environmental monitoring are concentrating their research on different "properties" of the environment, so that different types of monitoring have been delimited and further developed:

- *Geophysical monitoring* – surveying geophysical modifications registered as a consequence of the pollution and/or other influencing natural or anthropogenic factors
- *Chemical monitoring* – surveying the chemical composition changes occurring in the environment
- *Biochemical monitoring* – surveying the biochemical changes also occurring in the environment

Due to the complexity of the environmental compartments the chemical monitoring has always an interdisciplinary approach, being a team work with specialists with different backgrounds: chemists, biochemists, biologists, environmentalists, hydrologists, meteorologists, geographers, statisticians, ICT specialists, physicists, toxicologists, epidemiologists, and others. The following presentation will focus on the chemical monitoring, mainly on the analytical process of samples from different environmental compartments: *air, water, soil*.

2.2. COMPLEX CHARACTERIZATION OF POLLUTED SAMPLES

For the specialists involved in the ERA development the most relevant monitoring information is compulsory to complete the assessment schemes, but the providing data is a very complex activity, and this is what the following will present: what means and involves the "complex characterization of polluted samples". Some definitions and delimitation are considered to be important, as follows.

Sample is a portion of a system (environment), representative for the sampling place and moment. Samples are complex homogenous systems (solutions) or heterogeneous ones. Rarely we analyse a monocomponent sample, in most of the cases, the real samples are multicomponent systems, consisting in compounds that are present as major component, or as trace components.

Component/substance is a portion of the matter delimited by a specific elemental composition and having attributed a specific chemical formula.

Analyte represents the component of interest that is subject of analysis.

Samples are subject of *analysis*.

Components/substances (*analytes*) are subject of *determination*.

Sample characterisation consists in its components determination based on measurements; there are three different levels of components characterisation:

- *Structural analysis* – responds to the question "how the sample is structured?"; it is not specific for the environmental samples, only when the sample structure is relevant for further considerations (i.e. soil structure).
- *Qualitative analysis* (identification) – responds to the question "what individual components are present in the sample?"
- *Quantitative analysis* (quantitation) – responds to the question "how much identified component is present in the sample?"; *quantitative characterisation* of the sample implies the determination of each component concentration, only after a correct identification.

Sample concentration versus component concentration: we do determine and express the "component concentration" in the sample, meaning that the expression of "sample concentration" is not correct.

Component concentration means *any* report between the analyte (A), expressed in different modes (as mass, quantity, volume) and the sample (S) where the component is present, also expressed in different modes (as mass, volume), as presented in Table 1.

TABLE 1. Typical concentration types used for the quantitative determination of compounds.

Concentration type	Meaning	Application
Mass percentage concentration (%)	100 mass of A/mass of S	Liquid or solid samples
Volume percentage concentration (%)	100 volume of A/volume of S	Gaseous samples
Molar concentration (mole/L)	Moles of A/volume of S	Liquid samples
Normal concentration (equivalents/L)	Equivalents of A/volume of S	Liquid samples

For environmental analysis some atypical expressions are also used, according to different standards/regulation:

- $\mu g/m^3$ (air)
- *ppm*: mg/kg; µg/g (soil, biota); mg/L; µg/mL (water, biological fluids)
- *ppb*: µg/kg; ng/g (soil, biota); µg/L; ng/mL (water, biological fluids)

The complex characterisation of a sample is due to its specific properties:

a. *Aggregation status* depends on the substances composition and differs in the environmental compartments: *gaseous* (air, emissions); *liquid* (water, leaches, biological fluids); *solid* (soil, sediments, sludge, biota).

b. *Nature/origin* of the compounds is very much linked to the compounds composition and structure: *mineral* (inorganic); *biological* (organic).
c. *Composition*: mono-component; multi-component, homogeneous solutions (air, water) or heterogeneous systems (aerosol, smoke, soil, sediment, sludge, biota).
d. *Hydrophobicity* deals with the solubility of the compounds: water soluble (hydrophilic); water insoluble (hydrophobic).

The four criteria presented above are not the only ones that could have any relevance in influencing the complexity of an environmental sample, but we consider these to be more important. Considering at least these four criteria it is obvious why the characterisation of an environmental sample is a complete and rigorous process, requiring minimal initial knowledge about the sampling site and composition.

2.3. CHEMICAL MONITORING

Typical samples and possible polluting compounds that differ when air, water or soil are monitored, are given in Table 2. The table is not presenting the regulated monitoring parameters, but the expected groups of compounds, according to the diversity criteria listed above: aggregation status, sample nature and compounds origin, composition and hydrophobicity. Taking into account all these characteristics of the analytes, chemists are normally predicting at least the group of compounds possible present in environmental samples. To be noticed that the compounds possible to be found in water and soil samples are almost the same, due to the so called "soil solution" that contains most of the water soluble substances spread in the soil interstitial zones.

TABLE 2. Typical samples and compounds present in air, water and soil.

Specific samples (→) possible polluting compounds (↓)	Air	Water	Soil
	Gaseous air, aerosols, smoke, clouds, rain drops	Surface and ground waters, icebergs, wastewaters	Soil, sediments, sludge
Inorganic gases	O_2, CO_2, CO, SO_x, NO_x, Cl_2, H_2S, HCl	Dissolved oxygen (DO)	Dissolved oxygen (DO)
Anions	Nitrite, nitrate, sulphide, chloride, acetate		
Heavy metals cations	Very rare	Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+}, Fe^{2+}	
VOCs[a]	VOCs	Rare	Very rare
POPs[b]	POPs	PAHs[c], PCBs[d], pesticides, explosives	
Other	Particulate matter	Detergents	Detergents, humic/fulvic acids

[a] volatile organic compounds; [b] persistent organic pollutants; [c] polyaromatic hydrocarbons; [d] polychlorinated biphenyls.

3. Analytical Process for Environmental Monitoring

The analytical process consists in a sum of on-site or in-lab operations, done in order to obtain a qualitative and quantitative characterisation of complex samples. The main groups of operation are sampling, measuring and data processing, so that complete and reliable information should be further deliver (Chirila and Draghici, 2003). Most of the environmental analyses are regulated by standards, starting with the sampling procedure, analytical methods applicability and ending with the data processing and final result announcement. But, sometimes the sample might be more complex than the available standards. Moreover, the standards are conventionally established for a certain period and they are subject to reviewing from time to time, depending on the analytical methods and equipments development. The aim of the following paragraph is to present the *basic principles* of the sampling and analytical procedure and no the European or other international environmental standards. We consider that understanding the principles of all these procedures, will contribute to the adequate use of them, to the correlation of all the available information.

3.1. SAMPLING

Sampling is the generic term consisting in two distinguished groups of operations (Dobrinas et al., 2008): (1) *pre laboratory operations* (on-site sample up-take, on-site conservation, transportation and deposit); (2) *in laboratory operations* (sample pre-treatment and preparation for analysis. Sampling depends on some properties of the analytes or sample complexity, as well as on the laboratory quality requirements: available standards, equipment, reagents and reference materials, or specialized personnel (Chirila et al., 2006).

3.1.1. *Pre-laboratory Operations*

For the compounds that could suffer considerable transformations during the transport to the laboratory, samples should be analysed on-site, with adequate equipment, mainly based on specialised selective sensors and reagents kits. This type of information are very valuable, but the available equipment is not enough sensitive and precise for trace analysis. For the compounds that are either stable or can be preserved during the pre-treatment period, conservation procedure is used. From the sampling site, conserved samples are transported to the laboratory and deposit. These stages and operations are done according to standards (if available) and all the information (sampling place, time, conditions, personnel, conservation conditions) should be carefully registered to be further used for the final result formulation.

3.1.2. *Sample Pre-treatment*

Sample pre-treatment is a pre analysis stage, aiming to bring the sample and the analyte in a *measurable form* and involves operations that affect either the entire sample or the analyte:

- *Operations affecting the sample* – drying, weighting
- *Operations affecting the analyte*:
  a. *Dissolution* – is based on the analytes solubility properties.
  b. *Concentration, dilution* – depends on the analyte concentration in the sample.
  c. *Derivatisation* – consists in the analytes chemical transformation in a new chemical compound, adequate to the measurement and/or detection systems.
  d. *Purification, separation* – is done in order to distinguish the analyte(s) of interest from the rest of the compounds, co-existing in the sample; these "impurities" might introduce interfering information, similar to the analyte(s) of interest, thus contributing with errors and uncertainty to the final result; moreover.

Based on the complexity of the sample, the analyst will choose the most adequate pre-treatment operations, unless they are subject of standardisation.

3.1.3. *Separation Method Used in the Sample Pre-treatment*

Most of the operations used in sample pre-treatment are based on separation processes and there are several modes to classify and group them. The classification we propose is based on different phase equilibrium:

- *Gas–liquid*: absorbtion, purge and trap extraction, head space extraction, distillation, liophilization
- *Gas–solid*: adsorption, purge and trap extraction, head space extraction
- *Liquid–liquid*: solvent extraction, cloud point extraction, supercritical fluids extraction
- *Liquid–solid*: filtration, centrifugation, adsorption, ion exchange, precipitation, solid phase extraction (solid phase microextraction, solvent extraction, Soxhlet extraction, sonication extraction, microwave assisted extraction)

All these processes are contributing to the separation of some specific analytes from the rest of the matrix. The separation operations are nowadays developing in terms of method (principle) and technique (equipment) because analysts realised the importance of the sampling (including the pre-treatment phase) to the measurements and data processing. Only an adequate pre-treated sample could ensure a limited uncertainty of the final result.

From all the possible polluting compounds given in Table 2, we will further consider of interest for environmental monitoring two main classes of pollutants to be presented with examples of typical sampling procedures for chemical analysis: (1) heavy metals cations (from the inorganic class); (2) organic compounds, generically grouped according to their specific composition (PAHs, PCBs), specific properties (VOCs, POPs), or specific use (pesticides, detergents).

The analysts may use one pre-treatment method or another, considering different selection criteria based on performance characteristics: selectivity; specificity; precision and accuracy; reproducibility; recuperation.

3.1.4. *Sampling for Heavy Metals Analysis*

Sampling for heavy metals analysis is based on a very *simple principle*: to bringing the cations in a *soluble and stable form*:

a. Either monoatomic cations (Cu^{2+}, Fe^{2+}, etc.)
b. Or metallic compounds, where metallic atoms are linked to another group of atoms, forming different measurable species

Some procedures for heavy metals cations sampling are using water, strong acids or mixtures of strong acids, temperature, pressure or microwaves in order to dissolve the metallic insoluble compounds: simply dissolving in water (cold or hot water); wet digestion with strong acids (HCl, HF, HNO_3, $HClO_4$, H_2SO_4 with H_2O_2 or royal water); melting with fondants (NaOH or $K_2S_2O_8$); calcinations, followed by dissolving the ash in the above mentioned acids; dissolving at high pressure; microwave digestion. The other option to achieve the dissolving of metallic compounds is the use of some *reagents* capable to extract the metallic atoms contained in the insoluble substance and transform them in new soluble compounds:

- Chelating agents – forming complex ions (chelates) with the metallic cations
- Ion exchangers – changing their cations with those from the sample
- Surfactants – linking sample cations to a non-polar organic chain, changing their solubility and/or other properties
- Precipitation agents – transforming an insoluble (or soluble) compound to an (other) insoluble one, but easier to be dissolved with one of the above mentioned operations

As soon as the *soluble and stable forms of the analytes* (*heavy metals*) *are* obtained, their solutions are ready for chemical analysis.

3.1.5. *Sampling for Organic Compounds Analysis*

The sampling for organic compounds analysis is based on a similar *principle*, to extract them from the sample matrix in a *soluble and stable form*.

Due to the more complex structures of the organic compounds (compared with the inorganic ones), the extractions used in the pre-treatment stage are based on different physical properties of these analytes and/or of the adequate extractive reagents: phase equilibrium; adsorptive properties of some solid surfaces; absorptive properties of liquid and solid compounds; solubility of the pollutants in polar or non-polar solvents; modifications of the analytes at different energetic conditions: temperature, pressure, ultrasound or microwave.

Table 3 presents some typical extractive processes used for the organic compounds pre-treatment from liquid or solid matrixes. No matter the sampling procedure is used, adapted to the sample (matrix and compounds of interest), it is important that the strategy of the sampling process should ensure the chemical analyte integrity, or to use only those processes that provide controllable information, so that the analyst could make use of them.

TABLE 3. Extractive processes used for the pre-treatment of the organic compounds form different matrixes.

Sample matrix	Pre-treatment method
Liquid	Supercritical fluids extraction; liquid–liquid extraction (different techniques); solid phase extraction (different techniques); purge and trap extraction; head space extraction
Solid	Soxhlet extraction; supercritical fluids extraction; ultrasound assisted extraction; microwave assisted extraction

3.2. MEASUREMENTS

Chemical analysis of a sample consists in characterizing it from the point of view of its chemical composition and, in principle, is based on a measurable property of the solute (analyte) or solution (sample). Basically, as many measurable properties of the analyte or its solution will be identified and technically transferred to a measuring system, as many analytical methods will be developed.

There are two different "properties" to be discussed about (Table 4):

– *Property of the analyte* (physical or chemical) – is changed during the analysis process; is the bases of the analytical methods classification.
– *Measurable property* (measure) depending on the equipment that is able to indicate and register the changes of that measure; is the bases of the particular analytical methods classification.

TABLE 4. Classification of the methods for chemical analysis.

Analytical methods	Analyte property transformations	Measured property	Other observation
Chemical (classical)	Chemical (destructive)	Mass, volume, thermal, electrical, optical	Based on calibration curves $P = f(C_A)$
Physical	Physical (non-destructive)		
Physical-chemical	Combined		

The determination of the chemical composition of a sample imposes two type of information to be acquired: *qualitative information* (qualitative analysis, or identification); *quantitative information* (quantitative analysis, or quantification).

Quantitative analysis means to find the *measurable property* (*P*) that can be related as a function of the *analyte concentration* (C_A), based on physical-chemical laws: $P = f(C_A)$. No reliable quantitative information can be determined without a correct and complete qualitative characterization of the sample.

TABLE 5. Available analytical methods and their main applications.

Method	Method type	Measured property	Type of analyses	Concentration level
Gravimetry	Chemical	*Mass* of the pure analyte or of e compound with known formula	Quantitative	Major, minor
Titrimetry	Chemical	*Volume* of a standard solution (reagent react with the analyte)	Quantitative	Major, minor
Thermal analysis	Physical, chemical	*Physical/chemical transformation* of the analyte in thermal conditions	Qualitative, quantitative	Major, minor
Electro-chemical methods	Physical, chemical	*Electrical properties* of the analyte in solution	Quantitative, quantitative	Major, minor, trace
Atomic and molecular spectrometry	Physical, physical-chemical	*Wavelength and electromagnetic radiation intensity* emitted or absorbed by the analyte	Quantitative, quantitative, structural	Major, minor, trace
Mass spectrometry	Physical-chemical	*Mass/electric charge ratio* specific for the analyte or for some of its fragments	Quantitative, quantitative, structural	Major, minor, trace
Chromatography	Physical	*Repartition* of the analyte between two non-miscible phases	Quantitative, quantitative, structural	Major, minor, trace
Electrophoresis	Physical	*Mobility* of the analyte in electric field	Quantitative, quantitative, structural	Major, minor, trace
Radiometry	Physical	*Nuclear radiation* emitted by the analyte	Quantitative, quantitative	Major, minor, trace

The chemical methods (classical) were firstly developed, depending on technology development in time, and are based on chemical reactions that occur between the analyte and specific reagents, therefore they are destructive methods.

Physical methods are more recently developed analytical methods, based on physical transformation of the analyte, therefore are non-destructive. Sometimes a combination of physical and chemical transformation is required and the methods are thus called physical-chemical ones. Usually, a chemical pre-treatment of the analyte occurs (e.g. a derivatisation), followed by a physical property transformation.

The term of “instrumental methods” is sometimes used, defining the physical and physical-chemical modern analytical methods using specialised instruments. On our opinion, this term is nowadays out of use, because modern instruments (measuring systems) are also developed for classical (chemical) methods.

Table 5 synthetically presents some of the most used analytical methods, together with their applications, in terms of type of the analysis and of the concentration level of the analyte.

The *analytical methods* development diversification, in terms of mechanisms or equipment, allowed new *analytical techniques* development of the same method, meaning that the analytical technique is defined by same measurable property.

Gravimetry is a chemical classical method, which *principle* is based on measuring the mass of an analyte itself, or in most of the cases the mass of a product, obtained during a chemical reaction. Usually the reaction is a precipitation one, followed by filtering and drying the precipitate. If the reaction is carried out in electrolysis conditions, the mass of the compound deposit on the electrodes is measured (electro-gravimetry technique). If the reaction is carried out at high temperature conditions, the mass of the thermal decomposition compound is measured (thermo-gravimetry technique).

Titrimetry *principle* is based on measuring the volume of one of the solutions involved in the reaction of the analyte with a specific reagent (acid/base, redox, precipitation or complexing reagent), which define the related four techniques. Modern burettes are nowadays available, so that titrimetry should no longer be considered a classical method.

The electrochemical methods *principles* are based on measuring electrical properties of the analyte in solutions: *conductometry* (solution conductibility measurements); *voltammetry* (solution potential measurements); *potentiometry* (electromotric force measurements).

An important group of physical (physical-chemical) analytical method used for environmental monitoring is spectrometry, developed with specific techniques, according to different criteria, as presented in Table 6, for atomic (elemental) or molecular determinations (Cordos and Ponta, 2004; Franko et al., 2004).

TABLE 6. Spectrometric analytical methods and techniques.

Aim	*Methods* and techniques
Elemental analysis	*Atomic emission spectrometry* (*AES*): arc, flame, plasma (ICP), fluorescence *Atomic absorption spectrometry* (*AAS*): flame (FAAS), graphite furnace (GFAAS) X ray fluorescence
Molecular analysis	*Molecular emission spectrometry*: fluorescence, luminescence *Molecular absorption spectrometry*: UV-Vis, IR

Another group of analytical methods used in environmental analysis is based on complex information: *separation, qualitative, quantitative, as well as structural* (Table 7). Chromatography (Billiet, 2004; Dobrinas et al., 2008) and capillary electrophoresis (CE) are considered related methods: different from the analytical principle point of view (Draghici, 2002, 2004; Draghici and Billiet, 2004; Dobrinas et al., 2008), but similar form the point of view of the result display and data interpretation (chromatogram – electropherogram).

TABLE 7. Separation methods and techniques.

Separation methods	Separation techniques
Chromatography	*Gas chromatography* (*GC*) *Liquid chromatography* (*LC*): ion chromatography (IC); size exclusion chromatography (SEC); gel permeation chromatography (GPC); affinity chromatography (CA); chiral chromatography (CC) *Supercritical fluids chromatography* (*SFC*)
Electrophoresis	*Capillary electrophoresis* (*CE*): capillary zone electrophoresis (CZE); capillary electrochromatography (CEC); capillary gel electrophoresis (CGE); micellar electrokinetic chromatography (MEKC)

For environmental analysis, usually, standardised sampling and analytical methods are available, but sometimes the sample might be more complex or inadequate to the standard. In these cases the analyst is in the position to choose the most adequate method. The choice of the analytical method should take into account different evaluation criteria: depending on the sample; depending on the method performances and validation; depending on the analytical laboratory.

4. Conclusions

In order to achieve the exposure assessment and, finally, the risk assessment, monitoring data are required, either registered in specialised monitoring data bases, or especially done any time it is needed, for specific pollutants, areas and times. In the context of the exposure and risk assessment of chemical pollution in the environment, this paper presents where the data are obtained from, and how a complex characterization of polluted samples is done. We consider that for the non-specialists in chemical analysis, to whom the monitoring data are only tools to be used in different evaluations and assessment processed, basically knowledge on analytical process is required, for a better understanding of the environmental phenomenon. The dedicated literature is a comprehensive one, a lot of text books, monographs, peer review articles and other publications are available, but hard to be followed.

Therefore, our approach was a basic and simple one, describing in a condensed and systematic way the analytical stages, especially the principles of sampling and chemical analytical methods, to be a primary guidance, easily used by specialists not involved in such activities.

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MODELING OF CONTAMINANTS IN AQUATIC ENVIRONMENT

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Abstract. Integrated water management in river basins is accepted as a guiding principle in many countries, including Bulgaria. The challenges faced in watershed modeling have been reflected in the need to consider explicitly linkages among hydrology, geochemistry, environmental biology, meteorology, and climatologic variability. The shortage and pollution of fresh water require application of modern tools for solving the problems. For this reason, the application of technical aids in watershed planning and management is widespread in the world practice at present. Furthermore, due to the same reason public interest in the field of risk analysis, assessment and management has expanded recently. Risk analysis has emerged as an effective comprehensive procedure that supplements and complements the overall management of all aspects of our lives. Management of health care, environment and physical infrastructure systems, e.g. water resources, etc., acquires still greater importance. The use of mathematical models in this domain increases continuously. The application of water quality models is considered and the concept of water body integrity is described. This concept represents the main basis of many methods and mathematical models developed for determining the “real” water systems, so that a balance between the “functioning of water system” and “the impact of the water chain” is achieved. Fate models with or without a risk assessment component and ecotoxicological models are characterized in brief, and the points that should be clarified before entering the modeling procedure are outlined. It is pointed out that the complete solution of ecotoxicological problems requires in principal the consideration of four sub models. The results of modeling nutrient emissions in river systems are given, where main sources and pathways are taken into account to calculate the nutrient input into river systems by the MONERIS model, for example. They could be used for risk assessment of nitrogen and phosphorus export on watershed level.

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1. Introduction

Many countries accept to apply the approach of integrated water/water resources management in the framework of river basins. Watershed modeling in recent years has reflected the need to deal with spatial variability and scaling, and the need to consider explicitly linkages among hydrology, geochemistry, environmental biology, meteorology, and climatologic variability. The water shortage, pollution of fresh water and continuous water demand growth require application of modern tools for solving the problems more effectively. For this reason the use of technical aids in watershed planning and management is continuously increased at present. They are applied for many purposes and this gives the opportunity to complement knowledge in these spheres. The fresh water deficiency and anthropogenic impact on natural resources cause in the first place the water quality valuation. A number of substances discharged into water change its physical, chemical or biological properties. These contaminants change also the natural conditions of land and soil. The outcome of this situation could be expressed qualitatively and quantitatively as well as a loss, injury, disadvantage or gain. It is necessary that health care, environment and physical infrastructure systems, e.g. water resources, transportation, electric power, etc., should be analyzed together. This is the reason for the expanded public interest in the field of water management and risk analysis during the last 2 decades in particular. Risk analysis has emerged as an effective comprehensive procedure that supplements and complements the overall management of all aspects of our lives. When the substances are discharged into water, they change its physical, chemical or biological condition and then affect human health and environment. All problems related to the environment and human health are very complex due to the enormous number of many interacting components. The use of mathematical models is an attempt of capturing the most essential components and processes together, so that an adequate idea could be obtained about the current state of water resources, in order to evaluate the impact on it, to assess the created risk for human beings and environment today and in future and to develop and apply actions and legislative enactment for preservation and improvement of human and environmental health. Most of the mathematical models concerning water resource planning and management, especially water quality models, are developed on the base of the water body integrity concept and the factors affecting water quality. This concept is illustrated in Figure 1 (Novotny and Somlyody, 1995).

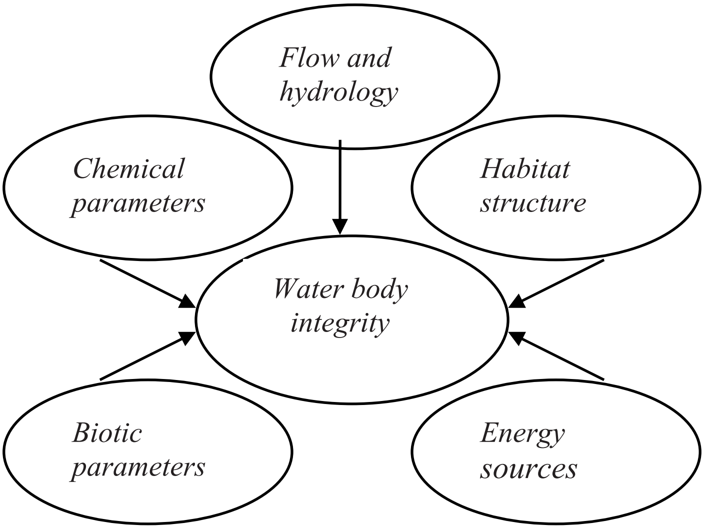

Figure 1. The concept of water body integrity and the factors affecting water quality.

The fate models with or without risk assessment components concerning water contaminants are also developed on these bases. Ecological models focus on the fate of toxic substances, i.e., where in the ecosystem the toxic substance could be found and in what concentrations. The complete solution of ecotoxicological problems requires in principal four sub models and they are considered below. The points that should be clarified before entering the modeling procedure are outlined, because they are crucial for getting reliable results and for selecting and applying different types of models. The results of nutrient emission modeling in a river system are shown, where the main sources and pathways are specified and are taken into account for calculating the nutrient input into river systems using the MONERIS model (Modeling Nutrient Emissions in River System). The results could be applied for many purposes as well as for risk assessment of nitrogen and phosphorus export on watershed level. This model is essential when the impact of nutrients should be evaluated on river basin scale and the risk assessment should be analyzed and managed.

2. Use of Water Quality Models

The use of technical aids in watershed planning and management can be intended for many purposes: to simulate and explain the functioning of systems, to simulate the runoff and water quality in watersheds, to predict effects of activities, to make risk assessments, to support decision making, and for direct control purposes. There has also been a growing use of technical tools for control of water systems behaviour, par example for dams, pumps, controlled inundation areas, etc. (Staes, 2005).

All problems related to the environment/water are complex problems due to the enormous number of many interacting components. The models attempt to capture the most essential components and processes involved in a problem, but usually they include only the most important ones, allowing simplification of environmental systems, so that fruitful results could be obtained. Models have been used in science and technology, but environmental modeling is a particular challenge due to the many interacting components in an ecosystem. Actually, for effective application of models, only the most essential mass and/or energy flows for the focal problem should be examined and the models for these flows and their related components should be limited.

The number of books and journals about development and application of conventional and toxic substance models for aquatic environment has steadily increased in the past 30 years. There are a number of articles with careful studies for applications in countries with different political, economic and social condition and extensive reviews on models have been presented – NATO ASI Series, Water Resources Research, Water Science and Technology – Water Quality International '98, etc., Dimitrova and Kosturkov, 1987, Biswas et al., 1990, Kosturkov and Dimitrova, 1992, Novotny and Somlyody, 1995, Haimes, 2004 and so on.

Water and water resource management, in particular, are undoubtedly one of the areas where numerous mathematical models have been developed and applied. A well known general classification of models, frequently used in this domain is:

- General theoretical background of the models (Basic theory)
- Biological Oxygen Demand (BOD) – Dissolved Oxygen (DO) models: the traditional "oxygen sag" curve and two more sophisticated versions
- Dispersion–advection models: a one dimensional pollutant–spill model version and a 2D transversal mixing model and
- Lake eutrophication models: spanning from simple experimental regression models to dynamic algae–phosphorous models, including a sub-model for input load calculation and lake water budget (regulation) model

The models considering toxic contaminants content and their impact on human and environmental health are developed on a quite good level, but their application in some countries, including in Bulgaria, is very limited for lack of input data and relevant experts for the particular cases. This is one of the reasons that a lot of models incorporate only fundamental water quality components and processes to characterise carbon, oxygen, nitrogen, and phosphorus (C, O, N, and P) cycling instead of biochemical oxygen demand as used in traditional models.

The processes and components of importance may be taken care of through calibration of the models. Calibration is understood as the process where the model outputs are tested with measurements from the focal system (aquatic and all other components of an ecosystem) and it is allowed to change a number of previously selected parameters within some indicated realistic ranges. Mainly, parameters known with the smallest certainty from literature or previous studies are selected for calibration, and by changing these parameters in realistic ranges, it is possible to a certain extent to make account of the processes and the components that are not included in the model due to their importance. If the calibrated model responses are in good agreement with the data, they may be used as scenario generators in a general strategy to conserve or improve the water quality.

The development of models must always contain at least six elements:

- *Conceptualization*, usually representing a diagram showing the relationship between components and processes.
- *Translation* of the conceptual diagram into a set of mathematical equations.
- *Verification*, where the internal logic of the model is tested.
- *Sensitivity analysis*, where the sensitivity of the most crucial components to changes in model input parameters and equations is found.
- *Calibration*, where a number of selected parameters are changed to improve the fit between observations and model output.
- *Validation*, where the model is tested with an independent set of data without any change of the parameters. The validation gives the modeler the opportunity to express the accuracy of the model to cope with the examined case study.

It is preposterous to develop models in a vacuum of knowledge. Models of conventional and toxic substances in our environment can only be developed, if there is good data and basic knowledge about the most frequent processes for these substances in ecosystems gained from detailed case studies. The case studies should include not only existing information but also the information from a provided field study. The selection and application of models is a very specific task and should be carried out very carefully, by skilled people. All information for water systems should be considered not only as a figure, as statistics. Thus all cases could be solved successfully, even if there are some data gaps, with the aid of modeling, provided sufficient preliminary research and appropriate simplification are made.

3. Fate of Conventional and Toxic Contaminants in Aquatic Environment

Traditionally, the class of conventional pollutants expressed integrally like BOD/DO and nutrients have received most attention from water quality planners although in recent years growing concern has been focused on the class of toxic pollutants. Concentrations of conventional pollutants are usually expressed in mg/l, toxic pollutant are expressed in µg/l or smaller units depending mainly on the threshold values of contaminants creating risk for human beings and environment. Conventional pollutants are mostly transported in dissolved or colloidal form. A fraction of conventional pollutants may be adsorbed on sediment particles, e.g. phosphorus and ammonia, and is usually not available to the resident biota. In slowly moving receiving water conventional pollutants, e.g. organic solids, associated with point sources, settle and are usually deposited within a short distance of the outfall and may cause problems by resuspension or by exerting a sediment oxygen demand.

Toxic pollutants may be strongly sorbed by suspended and benthic layer sediments. They may also undergo biochemical transformations, but the final products of such transformations may still be toxic or even more toxic than the original compounds. The residence time in the system of these compounds may be in the order of years, depending on the hydrodynamic characteristics of the water bodies and their chemical properties. It has been determined that sorption processes on sediments are important for 60 out of 129 priority pollutants and negligible for 28, while there is still uncertainty for the others; volatilization processes are important for 52 pollutants, not important for 44 and uncertain for the remaining ones.

The European Union (EU) list of priority substances is a new strategy against water pollution. The European Commission came to this decision establishing the list of priority substances, No. 2477/2001/EC, Annex X of the Water Framework Directive 2000/60/EC. This list includes 33 priority substances, as follows:

- Eleven priority hazardous substances: emissions, discharges and losses should be ceased not later than in 20 years.
- Fourteen priority substances under review: proposal by the EU-Commission by latest December 2002 which ones are priority hazardous.
- Eight priority substances: progressively reduce the discharges, emissions and losses.

Nevertheless the identification of all priority contaminants and the risk analysis, assessment and management will continue to require special care.

4. Processes Affecting the Fate of Contaminants in Water Bodies

The processes that affect the fate of contaminants, both conventional and toxic, in the aquatic environment usually are classified into four main categories:

- *Transport processes*, which include the following mechanisms: advection, sedimentation, volatilization and precipitation/dissolution.
- *Transformation processes* include biodegradation, hydrolysis, photolysis and oxidation or reduction.
- *Speciation processes* are acid-base equilibrium and sorption.
- *Bioaccumulation* refers to the intrusion of non-degradable, non-assimilable (usually toxic) compounds in the food chain. It is the final step in the pathway of pollutants in aquatic environment.

Most complex surface water quality models are constituted by at least two complementary units:

- A hydrodynamic model that is first used to determine flow conditions in the water body and
- A water quality model that will simulate the processes affecting water quality constituents according to the flow and velocity conditions in the water body

For modeling priority pollutants the sediment movement component must be included. In simpler cases, the hydrodynamic modeling part of the simulation can be substituted by knowledge of the appropriate flow and velocity fields in the water body under critical conditions, for instance from statistical analysis of historical records.

5. Fate Models With or Without a Risk Assessment Component

There are fate models with or without a risk assessment component. The former refer to conventional pollution, the second are a type of models focused on the fate of toxic substances, i.e. where in the ecosystem will the toxic substance be found and in what concentrations.

The complete solution of each eco-toxicological problem requires in principle four sub-models, from which the fate models may be considered to be the first models in the chain as shown in Figure 2. The four presented components are (Morgan, 1984): fate models, effect models, human evaluation models and human perception models. The first two sub-models are in principle “objective models”, predictive models, while the latter two are value oriented. The development of these sub-models is based on physical, chemical and biological processes and they are very similar to other environmental/water quality models and are based on mass transfer, mass balances, physical, chemical and biological processes. The second sub-models require accurate knowledge for the effects of toxic components. They are different from the generally applied environmental/ water quality models and cover risk assessment.

During the last 20 years researchers have developed understanding about the processes, by which people actually perceive exposures and effects of toxic chemicals, but these processes are just as important for risk assessment as the exposures and effects processes. The characteristics of risk and effects are of importance for the perceptions of people.

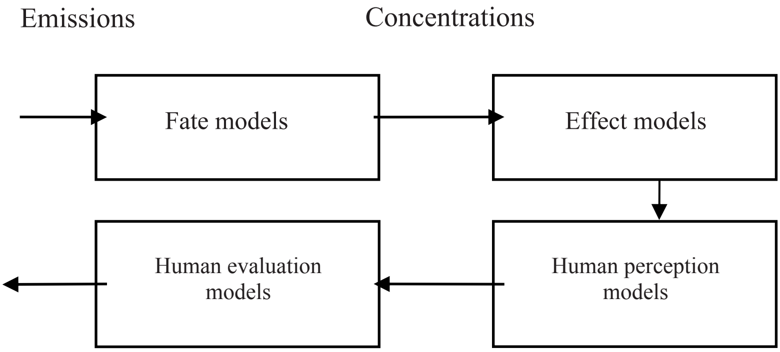

Figure 2. The four sub-models of integral eco-toxicological models.

6. Risk Characterization

The characterization of a risk is made on the base of information completed after a detailed investigation for the reasons that create it, the effects exerted by it on people and environment, and the possibilities for its elimination and management. Very often in practice different types of questionnaires are used.

They should be filled in after the following questions are answered:

- Is the risk voluntary or involuntary?
- Are the levels known to the exposed people or to science?
- Is it novel or old and familiar?
- Is it common or dreaded (for instance does it involve cancer)?
- Does it involve death?
- Are mishaps controllable?
- Are future generations threatened?
- Is the risk global, regional or local?
- Function of time/How (whether for instance increasing or decreasing)?
- Can it be easily reduced?

When the characteristics of effects should be done, the following questions have to be answered:

- Are the effects immediate or delayed?
- Do they affect many or a few people?
- Are they global, regional or local?
- Do they involve death or not?
- Are effects of mishaps controllable?
- Are they observable immediately?
- Is there a function in time?

For the development of risk management systems, first of all, as many characteristics listed above as possible, including human perceptions of these characteristics in the model, should be considered. It is also not necessary to focus too narrowly on certain types of risks because this may lead to sub-optimal solutions. An attempt has to be made to approach the problem as broad-mindedly as possible and to choose strategies that are pluralistic and adaptive. Benefit–cost analysis is an important element of the risk assessment management model, but it is far from being the only important element and the uncertainty in evaluation of benefit and cost should not be forgotten. Multi-attribute utility functions should be used, but one has to remember that people in general have troubles in thinking about more than 2–3, at the most 4, attributes in each outcome.

Because of the character of eco-toxicological models it is recommended that several points are clarified before entering the modeling procedure:

- Obtain the best possible knowledge about the processes of toxic substances under consideration.
- Attempt to get parameters of the toxic substance processes in the environment from the literature.
- Estimate all parameters.
- Compare the results from 2 and 3, and attempt to explain the discrepancies, if present.
- Use widely sensitivity analysis to estimate which processes and state variables would be feasible and relevant to include into the model.

These five stages of the modeling procedure should be also passed, in fact, before entering the procedure for modeling all kinds of contaminants as mentioned above in some different way.

7. Modeling Nutrient Emissions in River System, the MONERIS Model

Most diffuse nutrient emissions from the watershed originate from agricultural practices. Nutrients reach the fields through natural deposition, manure additions, and fertilizer applications. Nutrients are removed through harvesting. Nutrients (nitrogen and phosphorous) are considered to be conventional pollutants, but the impact of excess reactive nitrogen on environmental quality and ecosystem services is significant. Once in a reactive form, nitrogen is transported easily between air, water and soils in what is known as the nitrogen cascade. Since it can move so easily from the atmosphere, into soils and onto other surfaces, into waterways, and back again, a single nitrogen-containing molecule can have a series of impacts on the environment. In the air, it can contribute to higher levels of ozone in the lower atmosphere, causing respiratory ailments and damaging vegetation. From the atmosphere, it generally falls to the surface in acid deposition, generating a series of effects – corrosion of buildings, bridges and other human-made structures, acidification of soils, and inadvertent fertilization of trees and grasslands, creating unnatural growth rates, nutrient imbalances, and ultimately decreasing ecosystem health and biodiversity. Leaching out of the soil, reactive nitrogen can pollute groundwater and surface water, rendering it unfit for human consumption. Reactive nitrogen also promotes eutrophication in coastal ecosystems, ultimately reducing biodiversity due to a lack of oxygen needed for the survival of many species of aquatic plants and animals. The nitrogen cascade is interrupted only when reactive nitrogen is stored in inaccessible places or converted back to N_2 gas through denitrification. Making the nutrients balance is very important especially in rural areas, because both deviations from the equilibrium have negative consequences not only for the environment, but also for the health of people and animals. On the base of it exposure and assessment of nutrient (nitrogen and phosphorous) pollution could be made.

An example for Modeling Nutrient Emissions in a River System and the results from the application of the MONERIS model is given below. The model is applied in the Lesnovska River basin. The Lesnovska River is a third order tributary of the Danube River. It mouths into the Iskar River that flows into the Danube River. The catchment area of the Lesnovska River is 1,100 km^2. The river is 19.8 km long. The river basin comprises seven municipalities. Four of them belong to the Sofia City, the capital of Bulgaria, and the rest are in the Sofia region county. The nitrogen emissions in the Lesnovska River basin are mainly from the slag tailing dam effluent formed by the Kremikovtzi metallurgical plant, located in this area. The largest contribution to the phosphorus emissions comes from erosion, followed by loads from urban areas. The detailed case study was carried out in the framework of the project funded by the 5-th Framework Program of EU (Kosturkov et al., 2005). The objectives of this study were:

- To check the applicability of the nutrient balance module of the MONERIS model to the Lesnovska River basin
- To develop water and nutrient balances for the Bulgarian case study region employing the MONERIS model and

- To assess results through comparison of the calculated and observed river nutrient loads

For the achievement of these objectives and for the application of the MONERIS model a data base has been developed, which contains:

- *Digital maps* (DEM, soil map, land use map, administrative boundaries, catchment and subcatchment boundaries, river network, hydrogeological map, location of monitoring stations, location of WWTPs and industrial discharges, etc.)
- *Statistical information for agriculture* (crop statistics, mineral fertilizer application, forage production, livestock number)
- *Waste water statistics* (population served by sewer systems and WWTPs, population served by septic tanks and pits, portion of different sewers, water quantity and quality data for municipal and industrial discharges, capacity and actual loading and treatment stages of WWTPs)
- *Monitoring data* (surface water quantity and quality, meteorological data, nitrogen and phosphorus atmospheric deposition) and
- *Soil data* (texture, concentrations of N and P in topsoil)

To provide reliable nutrient balance on catchment scale data precision was essential and for this reason, except for the available data sets offered by the National Monitoring System in Bulgaria, an additional sampling programme was realized in the Lesnovska River basin for the definite period, when nutrients were systematically analyzed. The sampling program was developed and performed in the Water Quality Laboratory of the "Problems of Water Resources Quality" department at the Institute of Water Problems of the Bulgarian Academy of Sciences.

The determination of the parameters: water quantity, temperature, pH, conductivity, dissolved oxygen, suspended solids, ammonium-nitrogen, nitrite-nitrogen, nitrate-nitrogen, and total nitrogen, ortho-phosphate-phosphorous, total phosphorous, and silica, was performed in the period from October 2001 to November 2002. Some other parameters as oxygen saturation, TOC, $COD_{K_2Cr_2O_7}$, chloride, etc., related to the Lesnovska River water pollution were also analyzed.

The nutrient balance in the investigated agricultural area was determined as a difference between inputs and outputs of nutrients (nitrogen and phosphorous) for the watershed. When the balance is compiled for a given area, the surplus and deficit of nutrients has to be calculated and evaluated. The surplus may be accumulated in the soil and eventually find its way to surface water via direct drainage (e.g. tile drainage), surface runoff, or subsurface runoff, or can infiltrate deeper into the groundwater flow system. The main sources and pathways taken into account for calculating the nutrient input into river systems by the MONERIS model in agricultural areas are given in Figure 3. The approach used for nutrients balance calculation enables the modeling of nutrient emissions in each river system situated in the rural areas and the effective water and environment management in case of nutrient pollution.

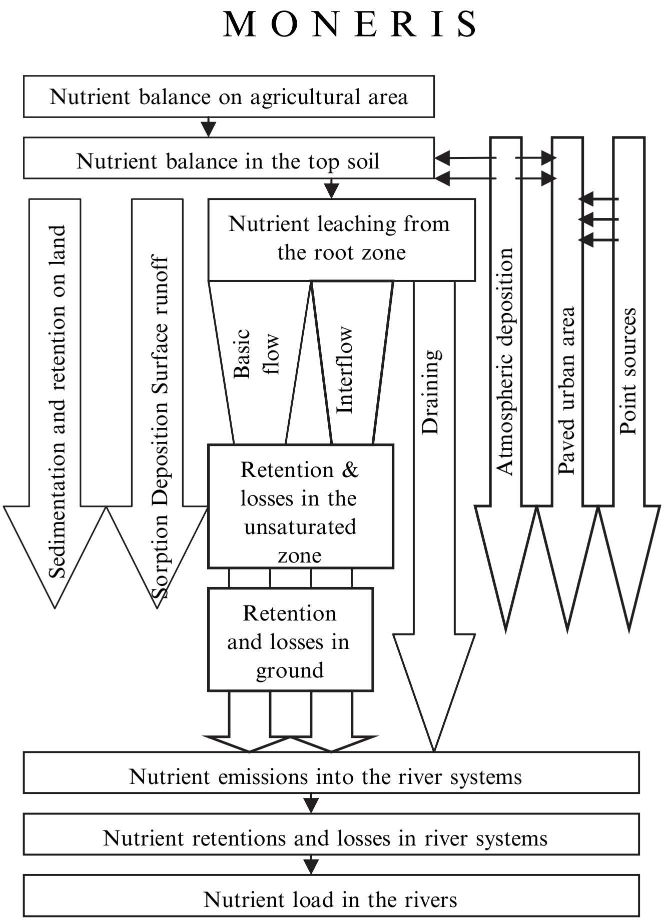

Figure 3. Main sources and pathways taken into account to calculate the nutrient input into the river systems by MONERIS model.

8. Conclusion

Modeling of contaminants in aquatic environment is widely used in the world practice for different purposes at present. Mathematical models are used to simulate and explain the functioning of systems, to simulate the runoff and water quality in watersheds, to predict effects of activities, to make risk assessments, to support decision making, and for direct control purposes. However in a number of countries, including Bulgaria, the application of models is extremely limited though the open source license to many of modeling systems. To encourage using of modern tools and technical information, it is necessary to exchange knowledge and experience, so that better understanding is achieved about when, where and how to implement mathematical models successfully.

A general review on water quality and ecotoxicological models is presented here. The use of water quality models is described and an aggregated classification is given for them. The main elements that must be always comprised in the model development procedure are outlined. Fate of conventional and toxic contaminants in aquatic environment and the basic processes affecting them are specified. Fate models with or without a risk assessment component and the specific features of water quality and environmental models covering risk assessment are explained. The procedure for characterization of risk assessment is described in more detail because it is a very important stage of the modeling procedure. An example for modeling nutrient emissions in river systems is given. This example illustrates the method applied for the main sources and pathways determination so that they could be taken into account in the calculation of nutrient inputs into the river systems by the MONERIS model. The developed data base needed for the application of the model is considered and substantiated.

The general review presented in this paper could contribute to expert activities in the application of mathematical models for solving a number of issues with respect to human and environmental health protection. Actually, the practice shows that all problems in pollution modeling could be solved with the aid of mathematical models only if a good preliminary study is carried out, the data needed are collected and processed in an appropriate manner and the adequate conceptualization, representing the relationship between components and processes, are clarified.

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TENTATIVE HAZARD ASSESSMENT OF INDUSTRIAL FACILITIES

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Abstract. Semi-quantitative risk assessment method was used for tentative evaluation of hazardous chemical waste incinerator. Data was collected using questionnaire involving five items as identification of installments, question regarding the technology, quality and quantity of hazardous substances, as well as environmental data. Site index was calculated from the information of technology and organisation. Dangerous substance index was calculated on the basis of hazardous properties and the quantity of chemicals stored or used on the facility. In the case of a chemical accident environmental components like distance to surface waters, sensitivity and vulnerability, permeability of soil number of public institutions, people living in the surroundings and economic factor were considered.

Keywords: environmental and health risk assessment, hazardous waste incinerator, vulnerability

1. Introduction

Major industrial accidents in the past decades draw attention worldwide to risks of industrial activities involving dangerous substances. These industrial accidents (such as Seveso, Bhopal, Sandos, cyanide pollution of Tisza river) caused huge devastation in human life, environmental and economical values as well. By eliminating consequences it appeared that both the authorities and citizens were unprepared for these events. Communities being at potential risk were not in possession of adequate information to avoid risks and did not have emergency plans either. Preparedness for industrial accidents is an intersectoral and complex task. The purpose of preparing emergency plans for chemical accidents

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is to minimize the consequences especially damages of human health (Convention Espoo, 1991). Local emergency plans are prepared by experts of the industry jointly with the authorities. These plans generally contain the scenario of potential accidents specifying the source of information and the rank of the hierarchy of decision making and execution. Each person involved in the emergency measures has to own the knowledge about the properties of the dangerous substances involved in the accident, quantitative and qualitative characteristics of the risks, the number of people potentially endangered and is responsible for the capacities and equipments of rescue to be assured.

Generally it can be stated that strategy for rapid intervention is lacking. Quantitative risk assessment requires lot of time and work. Therefore there is a need in application of rapid risk assessment methodology which integrates health and environmental aspects. World Health Organization and the Italian Ministry of Environment developed a method for rapid environment and health risk assessment methodology as an instrument for prevention of accidents and its consequences and drawing up emergency plans (Pilot project, 2000).

The semi-quantitative environmental and health risk assessment was made for the hazardous chemical waste incinerator plant in Komarom-Esztergom County, Hungary.

2. Method of Rapid Environmental and Health Risk Assessment

The process of rapid environment and health risk assessment is started from data collection. The questionnaire covers identification of facility, activity, technology data, hazardous substances, environmental and population data. It is followed by scoring and calculation of site index and dangerous substance index. Environmental properties like soil permeability, distance to surface water are also taken into consideration.

Data and information necessary to analyse risks was collected by co-workers of County Public Health Service using questionnaire. The checklist covered the type of activity, processing capacity, level of technology, operating conditions of plants, organization level, extension of the industrial site (m^2) and number of people in plant. The type of activity was defined according to the categories used in the Aarhus Convention (1998): oil refineries, gasification and liquefaction, power station, production and processing of mineral ore, production of non-ferrous crude metals, surface treatment of metals and plastics, chemical industry, incineration, chemical treatment, pipeline for transportation of gas, oil, chemicals, installation for storage of oil, petrochemical or chemical products.

The checklist contains also questions about surrounding environment, population, public institutions and economical values. Risk is evaluated from indices, namely Site Hazard Index, Environment and Health Vulnerability

Index and Site Accidental Risk Index. The range of variability of all indices is expected between 0 and 10 which allows comparison of partial and final results.

2.1. SITE HAZARD INDEX

Site Hazard Index is combined from three elements:

- The *site general index*, which is combined from Site Technological Factor and Site Organizational Factor with the following formula:

$$SGI = \sqrt{STF \cdot SOF}$$

where: SGI = Site General Index
STF = Site Technological Factor
SOF = Site Organization Factor

- The *dangerous substances index*, which is the quotient of the total amount of substance handled or stored in the site and the threshold quantity of the substance (determined in Seveso II Directive (1996) and relevant national legislation):

$$DSF = \sum \frac{q_i}{Q_i}$$

where: DSF = Dangerous Substance Factor
q_i = The quantity of the dangerous substance or summarized category of dangerous substances (falling within Seveso II Directive and relevant national legislation)
Q_i = The relevant threshold quantity of dangerous substances

Dangerous substances index (DSI) is determined from the above factor (DSF) according to the following formula:

$$DSI = 1/5x(DSF)$$

in case of $0 < DSF < 10$ or $DSI = 2x\log(DSF)$ in case of $DSF > 10$.

- Natural hazard index takes into account properties of the area where the plant was built as a potential flooding, earthquake or even instability of the soil can induce an industrial accident. Natural disasters increase hazard of the site. Each factor has a score 0 or 1, depending on occurrence of the event, then the sum of the three factors give the Natural hazard index with a maximum value of 3.

From the previous partial results Site Hazard Index is given by the following formula:

$$SHI = \sqrt{\left(\frac{[SGI + NHI] \times 10}{13}\right) \times DSI}$$

where: SHI = Site Hazard Index
SGI = Site General Index
NHI = Natural Hazards Index
DSI = Dangerous Substance Index
13 = Maximum value of SGI + NHI
10 = Normalizing factor

Site Hazard Index refers to the technology, dangerous substances and potential natural disasters of site. Higher is the value of the index higher is the hazard of the site. Ranking scale by site hazard is shown in Table 1.

TABLE 1. Ranking according to site hazard index.

Site hazard index (SHI)	Degree of site hazard
0–1.6	Low
1.6–3.6	Moderate
3.6–6.4	High
6.4–10	Severe

2.2. ENVIRONMENT AND HEALTH VULNERABILITY INDEX

Assessing environment and health vulnerability of the exterior area surrounding the site gives additional information about the consequences and effects of a potential accident inside the plant (Convention, Helsinki, 1992). Calculation of vulnerability takes into account all people potentially affected (workers inside the site, people living around the site); environmental elements and economical values in a circle of 5 km radius around the site. General Environmental and Health Vulnerability Index is combined from three partial indices.

2.2.1. *Population Vulnerability Index (PVI)*

Potential hazards of industrial plants can be divided into two parts from the point of view of the population: inhabitants living in the target area (a circle of 5 km radius around the site) as outer population, and people working in the site. Gravity of the consequences of an industrial accident mainly depends on the number of potentially effected people living outside but around the site which is characterized by Inhabitants Factor.

Vulnerability of the people working inside the site is given by Working People Factor which takes into account the number of the workers and the fact that they more likely suffer from the effects of an accident inside the site.

2.2.2. *Environmental Vulnerability Index (EVI)*

For calculation environmental elements potentially effected by the hazardous site: rivers (drinking water resources), lakes, soil (and its permeability) and groundwater (drinking water wells) were taken into account in vulnerability assessment of environmental media.

Wildlife and vegetation protected or other valuable ecosystems were also assessed.

2.2.3. *Economical Vulnerability Index (EVI)*

Economical targets as livestock, agriculture, aquaculture (fishing), industry and trade in the affected area potentially effected by the hazardous site the following are taken into account for the calculation.

2.2.4. *General Environment and Health Vulnerability Index (GEHVI)*

General Environment and Health Vulnerability Index is the combination of the partial vulnerability indices :

$$\text{GEHVI} = \frac{(10 \times \text{PVI} + 3 \times \text{EVI} + \text{ECVI})}{14}$$

where: GEHVI = General Environment and Health Vulnerability Index
PVI = Population Vulnerability Index
EVI = Environment Vulnerability Index
ECVI = Economical Vulnerability Index
14 = Normalising factor
10 and 3 = Specific weighting factors giving main importance to PVI – namely human life –, compared to other elements

Vulnerability is ranked by the following Table 2.

TABLE 2. Ranking according to vulnerability index.

General environment and health vulnerability index (GEHVI)	Degree of vulnerability
0–1.6	Low
1.6–3.6	Moderate
3.6–6.4	High
6.4–10	Severe

It is necessary to point out that inhabitants and workers are taken into account in the calculation with a higher emphasis to express importance of human life. It also means that if an industrial site is located near to (or in the middle of) an inhabited area the vulnerability of the surrounding environment will be high aside from any other property of the site.

2.3. ACCIDENT RISK OF THE SITE

To evaluate severity of an accident the classification and inventory of environmental and health components are selected on the basis of the gravity accounting criteria of Major Accident Reporting System (MARS, European Joint Research Centre).

Accident Risk Index refers to the area of 5 km radius surrounding the site. Calculating the accidental risk of the site the method simulates an industrial accident in which the gravity of the consequences of an accident at specific technical and environmental conditions can be determined (Kirchsteiger, 1998).

2.3.1. *Semi-quantitative Assessment of the Consequences of a Simulated Accident*

Consequences of each selected major accident can be determined with the use of simplified modeling tools with respect to acute and immediate effects.

Due to an accident dangerous substances are released into the environment in an uncontrolled manner. In order to identify the most representative case it is necessary to specify the “maximum releasable amount” of dangerous substances handled inside the establishment. For example this value may be the amount of the largest storage in a single vessel, tank or other equipment of the most dangerous substances or compounds. We assume that all of the maximum releasable amount might be suddenly released into the environment. Release to the atmosphere, soil, surface and subsurface waters are taken into account as routes of the spread of the contaminant.

In the case of dangerous substances released to the atmosphere as a result of an accident the methodology is based on the identification of the distances and area potentially affected and the inner and outer population.

To consider acute environmental and health consequences for liquid spills in waters the method takes into account the volume of water endangered, the maximum amount of dangerous substance might be released into the water, toxicological and chemical properties of the substance (LC50, persistency, bioaccumulation factor, octanol/water partition coefficient). For a liquid release to the soil the method has regard for the surface of soil contaminated by the release, the maximum amount of the dangerous substance might be released in the soil, and a coefficient of dispersion of the substance in the soil.

2.3.2. *Accident Risk of the Site*

Gravity of an industrial accident depends on the involved substances and the vulnerability of the environmental element(s) which the substances are released into. Environment in this context include human beings, different elements of the environment and the economical values. Higher is the number of inhabitants living around the site and of the economical and environmental values, higher is the vulnerability of the area so the gravity of the consequences of a potential accident will be higher as well.

Steps of determining accidental risk are the following:

An accident can be modelled for each substance which results in the distance (radius) and the surface of the effected area. The distance combined with a map of the site and the surrounding area is the basis of defining the gravity of the consequences to the population and environment:

$$\mathrm{EPGI} = \frac{10 \times C_P + 3 \times C_E + C_{EC}}{14}$$

where: EPGI = Environment and Population Gravity Index

C_P = Overall factor of gravity of the consequences for human beings

C_E = Overall factor of gravity of the consequences for environmental components

C_{EC} = Overall factor of gravity of the consequences for economical resources

10 and 3 = Weighting factors, in order to increase the importance of specific factor in global sum

14 = Normalising factor

The degree of gravity determines the value of accidental risk connected to specific dangerous substances and technical conditions (site hazard):

$$\mathrm{ARI} = \sqrt{\mathrm{SHI} \times \mathrm{EPGI}}$$

where: ARI = Single Accident Risk Index

SHI = Site Hazard Index

EPGI = Environment and Population Gravity Index

After the risk of all potential accident is calculated the highest accidental risk value will give the risk of the site according to worst case scenario:

$$\mathrm{SRI} = \max_{i}(\mathrm{ARI}_i)$$

where: SRI= Site Risk Index

Degree of the site risk can be determined by Table 3.

TABLE 3. Ranking according to site risk index.

Site risk index (SRI)	Degree of accidental risk of the site
0–1.6	Low
1.6–3.6	Moderate
3.6–6.4	High
6.4–10	Severe

3. Results of Rapid Risk Assessment of the Hazardous Chemical Waste Incinerator

Taking into account the large number of dangerous substances handled in the incinerator and the fact that chemicals are mainly in mixtures we used the maximum amounts in order to simulate the worst case scenario.

Site Hazard Index of the site is the combination of Site General Index, Dangerous Substance Index and Natural Hazard Index, the value is expected between 0 and 10.

TABLE 4. Substances involved in the rapid risk assessment.

Name of substance	Quantity (t)	Risk phrases
Methanol	10	11-23/24/25-39/23/24/25
Benzene	1	45-11-48/23/24/25
Dimethyl sulphate	1	45-25-26-34
1,2-Dichloroethane	2	45-11-22-36/37/38
1,2-Dichlorobenzene	0.5	22-36/37/38-50/53
Sodium cyanide	0.05	26/27/28-32
Sodium azide	0.05	28-32
Nitrobenzene	0.05	23-25
Tetrachloro ethylene	1	40-51-53
Toluene	10	11-20
Ethyl acetate	50	11-36-66-67
Ethanol	50	11
N-propanol	150	11
Acetone	150	11-36-66-67
Dangerous substance index	2.00	

Site Hazard Index characterizes the plant by its technology, organization, dangerous substances handled or used. Table 4 contains dangerous substances inventoried on the scene and the calculated dangerous substance index.

Small quantities of dangerous substances and high level of organization and technology produced moderate site hazard. It also should be underlined that Dangerous Substances Factor (quotient of the quantity of substances and the relevant threshold limit value) is the dominant element of the assessment.

As a result of the many kinds of dangerous substances which are present at a given time in the incinerator at relatively small quantities and also modern, reliable technology and high organizational level of the plant as well as the area not being threatened by natural disasters the value of Site Hazard Index became 1.84 accordingly degree of hazard is "moderate" (Table 5).

We have to point out that risk arising from incineration during emission was not analysed with this methodology. Rapid environment and health risk assessment method is suitable for the assessment of potential hazards of industrial facility.

TABLE 5. Characteristics of the incinerator.

Characteristics of the incinerator	Values	Explanation
Age of the incinerator	5	Between 11–30 years
Process control	1	Process control is high
Type of operation	1	Continuous production cycle (24 h, 7 days a week)
Operating conditions of plant	7	Processes utilizing high pressures or high temperatures (>10 bar or >100°C)
Loading/unloading	10	High number of operation (>300 a year)
Organizational level	1	High environmental and/or safety management system
Flooding subjected area	No	–
Seismic area	No	–
Soil instability, earth movements	No	–
Site general index	**2.19**	
Dangerous substances index	**2.00**	
Natural hazards index	**0.00**	
Site hazard index	**1.84**	Degree of hazard: Moderate

3.1. VULNERABILITY OF HUMAN HEALTH AND THE ENVIRONMENT

For identification of the vulnerability of human population and environment three groups of indices were used characterising human, natural and man-made environment. These indices consider number of workers and inhabitants, properties of environmental media and economical values. Inhabitants and workers appear with higher importance in the calculation. Vulnerability refers to the surrounding environment of 5 km radius around the site.

Summary of results and final indexes are shown in Tables 6–8:

TABLE 6. Values of the population characteristics.

Characteristics of the environment	Value	Factors (intermediate results)	Vulnerability index
Number of inhabitants	35,000	*Outer population*	
Critical centres:	One	*vulnerability factor*	*Population*
Hospital	More than 1		*vulnerability index*
School	More than 1	*9.40*	*5.36*
Social institution			
Workers of the plant (persons)	92	*Inner population vulnerability factor* *2.46*	

TABLE 7. Values of the environmental characteristics.

Characteristics of the environment	Value	Factors (intermediate results)	Vulnerability index
Rivers	More	*River vulnerability*	
Potable use	Yes	*factor1.50*	
Lakes and pods	0.6–5 km^2	*Lakes*	
Potable use	No	*vulnerability factor 0.60*	
Soil and groundwater	<50 km^2	*Soil and groundwater*	*Environment*
Soil Permeabiliy	Mean perm.	*vulnerability factor 1.80*	*vulnerability index 6.47*
Potable use of groundwater	Yes		
Wildlife and vegetation	5–50 km^2	*Wildlife and vegetation*	
Protected species	Yes	*vulnerability factor 1.25*	

GENERAL ENVIRONMENT AND HEALTH VULNERABILITY INDEX: 6.47 (All data and results consider the area of 5 km radius around the site.)

In accordance with the above results it can be stated that vulnerability of the surrounding environment of hazardous waste incinerator is high from the aspect of human beings, environmental and economical components.

TABLE 8. Values of the economical characteristics.

Characteristics of the environment	Value	Factors (intermediate results)	Vulnerability index
Livestock	More	–	
Agriculture	More	–	*Economical*
Aquaculture	More	–	*vulnerability index*
Industry and business (trade)	More	–	*10.00*

3.2. CALCULATING ACCIDENTAL RISK OF THE SITE

Accidental release of single chemical was simulated with REHRA software. The uncontrolled release of total amount of each substance was used to represent the worst case scenario and to be able to select substances require

TABLE 9. Single accident risk indices (ARI) and the site risk index calculated from ARIs.

Dangerous substances	Risk phrases	Amount of substance in the accident (t)	Radius of zone of high leathalty (m)	Radius of zone of serious damages (m)	Single Accident Risk Indexes (ARI)
Acetone	11-36-66-67	150	83	166	1.48
Ethyl acetate	11-36-66-67	50	25	50	1.48
Sodium cyanide	26/27/28-32	0.05	50	–*	1.62
Sodium azide	28-32	0.05	50	–*	1.62
1,2dimethyl sulphate	45-25-26-34	1	110	–*	1.62
Toluene	11-20	10	25	50	1.32
Ethanol	11	150	25	50	1.48
n-propanol	11	150	42	84	1.48

[*] Due to lack of toxicological data the evaluation is not complete. The zone of serious damages cannot be calculated without inhalational LC_{50} and IDLH values. As the results in the table show the consequences of most simulated accidents are expected within the establishment effecting mainly workers. Fatal accidents can also be expected in the inner population. In three cases – dimethyl sulphate, sodium cyanide, sodium azide – due to lack of data for calculation results are not complete, but in these cases distance of lethality and toxic properties indicate the hazard represented by these substances.

higher attention from the safety point of view. From another aspect using total amounts in the simulation was necessary for that identified dangerous substances indicate risks of different wastes received in the incinerator. Some of the substances were found to have negligible effects as the consequence of a simulated accidents because of the small amounts or having properties causing less serious impacts (e.g. in current case tetrachloroethylene, benzene, 1,2-dichloroethane, 1,2 dichlorobenzene, oxygen, nitrobenzene, potassium permanganate and perchloric acid) The following accidents involving dangerous substances were analysed: acetone, ethylacetate, sodiumcyanide, sodium-azide, methanol, dimethylsulphate, toluene, ethanol, n-propanol.

Results of each simulated accidents involving a dangerous substance are summarized in Table 9.

4. Summary of Rapid Environment and Health Risk Assessment

Integrated results (Site Hazard; Environment and Health Vulnerability and Site Risk) of risk assessment in the hazardous chemical waste incinerator are summarized in Table 10.

TABLE 10. Integrated results of risk assessment in the hazardous chemical waste incinerator.

Index	Value	Ranking
Site hazard index	1,84	*Moderate hazard*
Environment and health vulnerability	6,47	*Vulnerability is very high*
Site risk	1,62	*Moderate risk*

Site hazard is moderate according to the technological and organizational characteristics and the quantitative and qualitative properties of dangerous substances handled in the incinerator.

Surrounding area of the site is **very vulnerable** by the number of population, environmental and economical values of the territory.

Modeling some accident situations the **site risk is moderate**, consequences of simulated accidents are expected mainly within the site having more serious effects on the inner population (workers).

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ECOLOGICAL APPROACH TO EVALUATE EFFECTS OF CHEMICAL POLLUTANTS IN SOIL AND GROUNDWATER

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Abstract. Soil is the foundation of the entire biosphere, and the most important complex interface for the global transformation and interchange of matter and energy. Only a healthy, i.e., biologically active soil warrants the sufficient production of food for the growing human population. Under stress conditions caused, e.g., by a long-term dissemination of chemical pollutants, the development and biochemical activities of soil microorganisms which play a key role in ecologically important biogeochemical processes undergo several alterations. To prevent negative ecological consequences, microbiologically-related parameters should be involved in the indication of soil quality. After evaluation of more than 20 individual parameters we made a conclusion that nitrogen-fixing bacteria, total microbial biomass, soil respiration (CO_2 release), enzymatic activity (dehydrogenase), and in part also the humification activity of microorganisms could be used as indicators of soil quality. However, seasonal oscillations in the values of the individual parameters occurred, and should be appropriately respected in the evaluation of results achieved. Since groundwater represents a capital resource of drinking water in many countries, there is also a growing public concern with contamination of groundwater aquifers by different health relevant chemicals. Based on an expected ability of autochthonous microbial populations and other natural factors over time to bring about reduction or even elimination of health hazard for humans and animals, natural attenuation might stand for the remedy of contaminated aquifers. To be effective in transformation or degradation of chemicals, however, microorganisms indigenous to groundwater must be capable of resisting to chemical pollutants. In our laboratory experiments, microorganisms indigenous to an unpolluted deep groundwater aquifer were enriched, and in portions, the microbial biomass obtained was

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exposed to different organic chemicals in samples of groundwater. The effect of the chemicals on the size of biomass (ATP contents), and metabolic activities (dehydrogenase, and respiratory activity) was measured. The results indicate toxic effects to be predominantly caused by very high concentrations of the chemicals, sometimes even near to the full water saturation capacity. On the other hand, a few chlorophenols, anilines and some nitrated aromatic hydrocarbons demonstrated a high degree of toxicity at rather low concentrations.

Keywords: soil contamination, groundwater contamination, ecological assessment, microbiological methods

1. Introduction

In many locations, soils and groundwater aquifers suffer under chemical pollution. Since the application of sophisticated technologies for a clean-up of the contaminated sites at reasonable costs is hardly achievable in many areas, a natural attenuation has been repeatedly considered as the only practicable solution. By this altern.ative technology, biodegradation of organic pollutants and stabilization of inorganic ones should be achieved in course of long-term natural biological processes. For success to be achieved, however, there are two basic preconditions: (i) The on-site microbial population must be capable of surviving under contamination; (ii) the microbial enzyme activities must not be inhibited by the contaminants. In our laboratory experiments, we attempted to find out whether or not such preconditions exists in soil and groundwater contaminated by different chemicals.

2. Environmental Importance of Soil Organisms, and Effects of Anthropogenic Pollutants on Their Activities

For the main groups of soil organisms, the following numbers of species have been estimated by Pankhurst (1997): Bacteria 30,000; Fungi 1,500,000: Algae 60,000; Protozoa 10,000; Nematodes 5,000,000; Earthworms 3,000. From results of a restriction analysis of DNA extracted from soil samples, Torsvik et al. (1997) postulated that some 6,000 and up to 18,000 microbial species may exist in a single 1 g soil. In Figure 1 the linkages between different communities of soil organisms, their biochemical activities, and ecologically important processes such as mineralization and transformation of plant residues and other organic materials are shown.

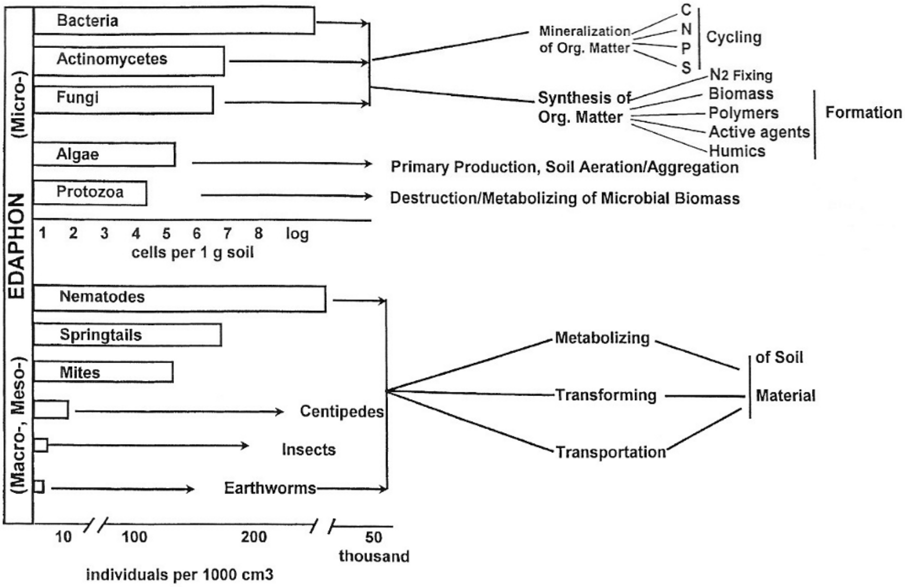

Figure 1. Main groups of soil organisms, their approximate counts and ecologically important activities. (From Filip, 2002.)

In a review based on numerous individual studies, Filip (1995) reported evident effects of chemical contaminants on (a) size and composition of soil microbial populations, and on populations of micro- and meso-fauna, (b) turnover of carbonaceous substrata, (c) turnover of nitrogenous substrata, (d) influences on enzyme activities, (e) degradation of plant residues, and (f) on the resistance of soil microorganisms against a heavy metal soil contamination. The author also emphasised the importance of site specific non-biotic factors that strongly influence the effectiveness of chemical contaminants on soil organisms and their metabolic activities. In a brief overview, the behavior of chemicals in soil, and their interactions with microorganisms are shown in Figure 2.

From the energetic point of view, mineralization of organic matter represents a catabolic process releasing energy for anabolic **(synthesizing)** activities of soil organisms. One can assume that anabolic activities of soil microorganisms may also affect the global cycling of carbon. Norby (1997) calculated, that only about 45% of the globally increased CO_2 production remains in the atmosphere while the main part is apparently missing. That missing carbon is proposed to be assigned to soil environments either into a labile, short-lived pool such as microbial biomass, or into a refractory soil organic matter such as humic substances. Thus, the assessment of anabolic activity of soil microorganisms, i.e., the estimation of a balance between C bound in soil microbial biomass and humic substances on the one hand, and the amount of CO_2 released from soil on the other hand, can effectively contribute to an objective evaluation of the global carbon budget.

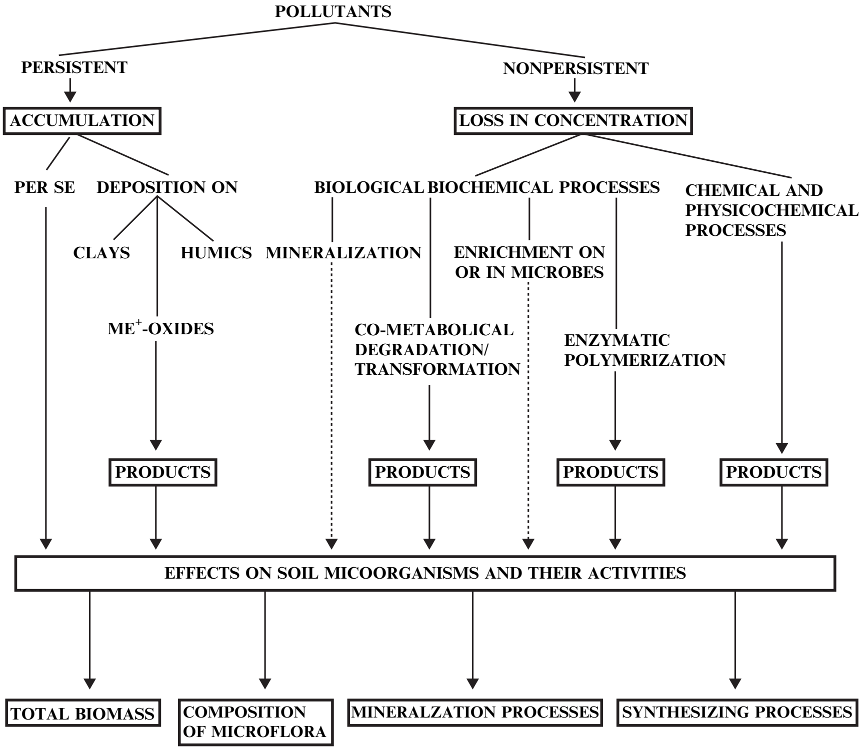

Figure 2. Behavior of pollutants in soil and their possible effects on microorganisms and ecologically important microbial processes. (From Filip, 1998.)

Among the major elements required for all forms of life, nitrogen is unique in that it exists in vast amounts in the atmosphere. From that stock, N_2 must be bound into a living matter by the activity of free-living and/or symbiotic microorganisms mainly in soils. For the enormous importance of the N_2 fixing in global cycle of nitrogen, its assessment should not fail in the evaluation of soil quality.

Beside the N_2-fixation, also other key processes of the N cycle, such as ammonification of nitrogen bound in organic compounds, oxidation of NH_4^+-N to NO_3^--N (nitrification), and reduction of NO_3/NO_2 to N_2 (denitrification), represent microbially mediated soil processes which can be used as indicators in ecologically based system of assessing soil quality. This is because an anthropogenic alteration of the above mentioned primary processes may have multiple consequences, such as (i) an increased concentration of the greenhouse gas N_2O and/or other NO_x gases globally, (ii) losses in soil nutrient, (iii) acidification of soils, and (iv) increased transfer of N from soil to aquatic environments (Vitousek et al., 1997).

Not only microbially mediated cycles of C and N may become strongly affected by human activities. Similar is true also for the S, P and other bio-elements. However, the key roles of C and N in the biosphere, and also an availability of well proved analytical methods may account for the priority involvement of C and N transformations in the biological assessment of soil quality.

In a soil artificially contaminated with Pb, a significant decrease in values of the individual parameters was observed (Figure 3), but on the other hand, in soil samples contaminated by mineral oil an evident increase of respiration activity was measured (not shown in Figure 3). A strong seasonal variability was observed even for the most sensitive parameter such as N_2-fixing bacteria. Their highest indicative sensitivity was measured in summer (June), and the lowest one usually in March.

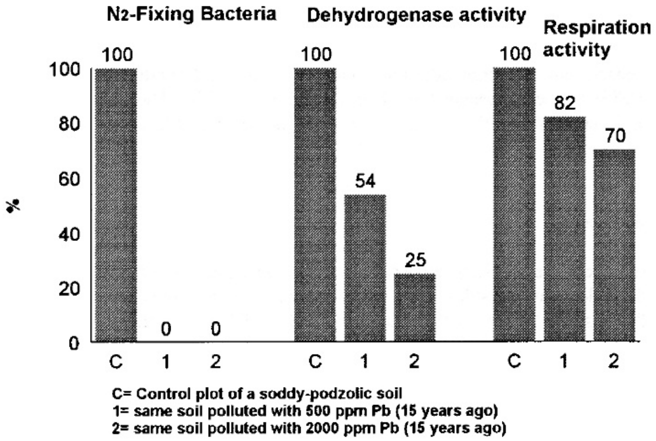

Figure 3. Relative values of N_2-fixing bacteria numbers, and dehydrogenase and respiration activities in a Pb-contaminated soil. (From Filip, 2002.)

In Figure 4, the most relevant biological and also physical-chemical parameters which should be respected in the monitoring of soil quality are presented. In Table 1 the relative sensitivity of the most reliable parameters is shown as observed in our experiments. Nitrogen fixing bacteria, the enzyme activity (dehydrogenase), and respiration activity (CO_2 release) appeared among the most sensitive methods to indicate anthropogenically caused soil stress. Sometimes, nitrification activity also appeared a useful indicator. It should be admitted that depending on the soil use, contradictory results were sometimes obtained, too. Mean amounts of soil biomass, e.g., were lower in contaminated meadow and forest soils as compared with control sites, and on the other hand, they were enhanced in arable and urban soils. Differences were found also in the capability of soil microbial communities to mineralize added substrate (lucerne meal) and in short-term changes in the contents and quality (optical density) of humic substances. The humification process was mainly suppressed in polluted soils where the most of the added organic substrate was either mineralized or remained non-utilized during an incubation period.

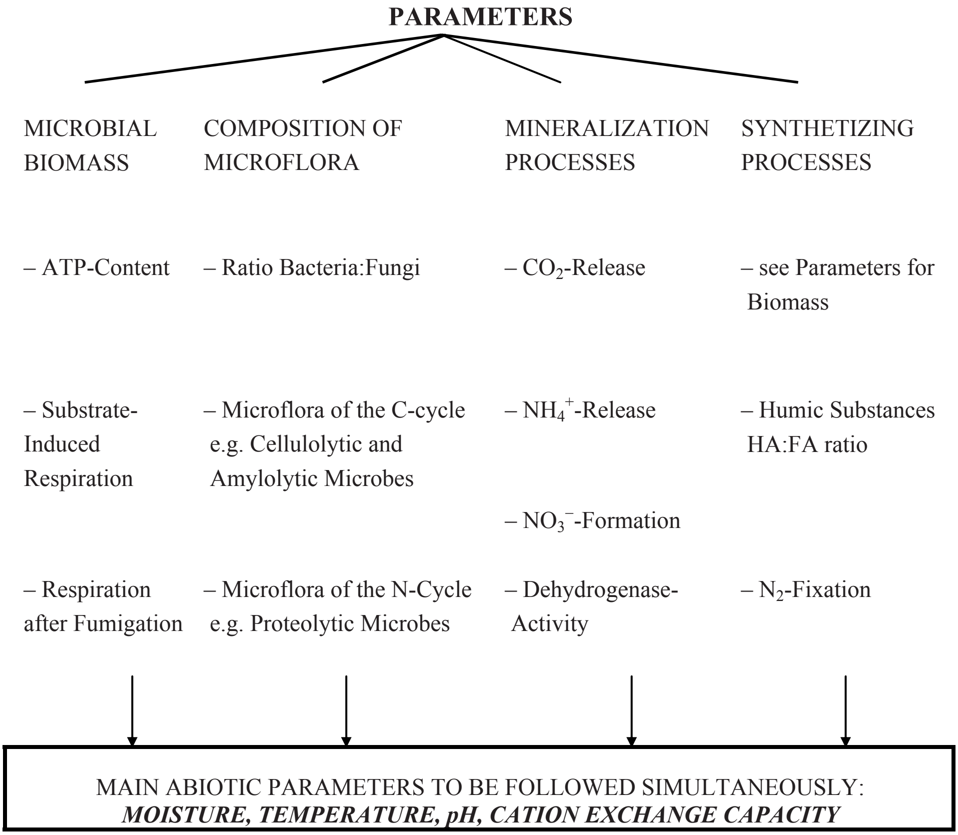

Figure 4. Selected parameters to evaluate effects of chemical pollutants on ecologically important soil characteristics.

In order to obtain data on biological aspects of soil quality quickly, several authors adopted different aquatic tests for soil quality testing (Kördel, 2000; Pfeifer et al., 2000). Water-born organisms such as algae, *Daphnia magna*, and also different freshwater fish have been recommended for use (Hund, 1994, Debus and Hund, 1997). Graefe (1997) and some other authors (see in: Vortragstagung, 1996) attempted to establish biological soil diagnostics on the classification, survival and/or behavior of soil invertebrates. Yakovlev (1997) preferred to evaluate the abundance of protozoa (*Amoebae, Colpodida*) and algae (*Heterotrix* sp.) in soil **samples** and also their behavior in a soil suspension as criteria for the characterization of virgin and human affected soils. Römbke and Moltmann (1996) recommended different tests which include soil saprophagous invertebrates, plants, pollinators, such as honey bees, and even higher vertebrates (birds, mammals) as indicator in the soil evaluation. Some of such test strategies might have an advantage because of their relative simplicity in use, and, perhaps, quite an easy standardization. However, such test procedures seem rather capable to oversimplify both biological and abiotic structural complexity and heterogeneity of soil, and mainly they disregard fully soil ecological functions.

TABLE 1. Relative sensitivity of microbiological and biochemical parameters for the assessment of soil quality based on long-term analyses from 49 differently anthropogenically affected soils. (From Filip, 2002.)

Parameter	Relative sensitivity[a]
Microbial biomass	+/++
Composition of microbial communities	
Copiotrophic bacteria (colony forming units)	+/++
Oligotrophic bacteria	++
Actinomycetes	++
Microscopic fungi	++
Proteolytic spore forming bacteria	–/+
Cellulose decomposer	+/++
N_2-fixing bacteria	++++
Pseudomonads	–/+
Biochemical process-linked activities	
Respiration (CO_2 release)	+++
Ammonification (NH_4^+ release)	++
Nitrification/denitrification	++/+++
Dehydrogenase activity	+++/++++
Humification activity	++

[a] Sensitivity (relative to control soil); – = No detected; + = Low; ++++ = Maximum.

TABLE 2. List of methodical approaches and tests to characterize soil ecological values. (Accommodated from Andren et al., 2004.)

Characteristics	Suggested tests
Microbial biomass	*Normalized tests*: ISO 14240-1 (substrate induced respiration) ISO 14240-2 (fumigation-extraction) *Calculated test*: Microbial quotient *Tests upon research*: Fumigation-incubation Specific group biomass (e.g., ergosterol determination for fungi) Physiological method (initial mineralization rate of glucose added) ATP method (adenosine triphosphate concentration in soil)
Microbial activity	*Normalized tests*: ISO 15685 (nitrification – NH_4 oxidation) ISO 14238 (N mineralization and nitrification – incubation method) ISO 14239 (C mineralization = respiration – incubation method) ISO 16072 (basal respiration of heterotrophs) ISO 17155 (respiration curves) *Calculated tests*: Respiratory quotient Fungal/bacterial respiratory ratio *Tests upon research*: Denitrification (e.g., N_2O production – anaerobic conditions) N fixation (e.g., C_2H_4 production – incubation – nitrogenase activity) Mycorrhizae (percentage of root colonized in a test plant)
Enzymatic activity	*Normalized tests*: ISO 23753-1 (dehydrogenase activity – TTC method) ISO 23753-2 (dehydrogenase activity – ITC method) *Tests upon research*: Enzymatic activity tests (other than dehydrogenase: phosphatase, sulphatase, peptidase, urease, esterase, cellulase, amylase, xylanase, laccase, peroxydase, maltase, saccharase, cellobiase) Enzyme index
Root pathogens	*Tests upon research*: Detection of root pathogens
Microbial diversity	*Tests upon research*: Community level physiological profiles (e.g., BIOLOG®-system) Nucleic acid analysis (e.g., soil DNA extraction and PCR, RPFT, DGGE) Dilution plating and culturing methods Ester-linked fatty acids estimation (e.g., PFLA, FAME, MIDI, SLB – chemical microbial signatures)

TABLE 3. Rating of effects obtained in ecotoxicological tests as related to unaffected controls. (Modified from Römbke and Moltmann, 1996.)

Rating	Mortality or lowered beneficence (%)	
	Laboratory tests	Semi-field and field tests
Not harmful	<50	<25
Slightly harmful	50–79	25–49
Moderately harmful	80–99	50–75
Seriously harmful	>99	>75

In Table 2 different methodical approaches and also some standardized tests are listed that could be currently recommended for ecologically based evaluation of soil quality. According to Zvyagintsev et al. (2002), data obtained by molecular genetic methods are much more ambiguous that those obtained by the culture techniques. The majority of soil microbial clones have a low degree of homology with the nucleotide sequences of the known bacterial taxa available in data-bases, and thus, they might be designated as new phylogenic groups. On the other hand, common soil inhabitants often cannot be detected. Furthermore one cannot obtain information on physiological peculiarities and ecological functions of soil microorganisms. Therefore the authors underline the necessity of further research in order to discover new views into soil microbial diversity and functionality by improving the existing and developing novel cultural techniques for use in a broad-scale soil monitoring (Filip, 2002).

The actual question to be further elucidated is that of critical limits for the individual biological and biochemical parameters of soil quality. For the evaluation of results obtained in the individual tests, the respective effects can be rated according their importance, and this in relation to values obtained in control variants that remained untreated. Römbke and Moltmann (1996) suggested respective percentages in a range as shown in Table 3.

A simple application of the suggested values, however seem not applicable for the evaluation of soil ecologic functions. Dahlin et al. (1997) demonstrated some difficulties in solving this problem on soils with a low level of heavy metals contamination, and Robertson et al. (1997) pointed on the fact that sometimes, different analytical data can be obtained even from **pedogenetic** homogenous soil sites. Specific solutions based on statistical methods have been suggested (Halvorson et al., 1996; Smith et al., 1993) but further methodological improvements in the soil quality testing should be also attempted.

3. Microorganisms in Groundwater as Affected by Chemical Pollutants

For our investigations, groundwater was collected from a deep waterworks well (31.8 m) in environs of Eppertshausen (Hesse, Germany). As recommended by Phelps and Fredrickson (2002) a simple procedures was used, i.e., clean, sterile glass bottles were filled with groundwater directly from well tubing. Prior to sampling, however, water was pumped for 3 h to make sure samples to originate from a pristine aquifer. The fresh filled bottles were kept at an ambient temperature (ca. 10°C) and transported to the laboratory without delay.

A PYGV medium containing peptone, yeast extract and glucose as carbon and nitrogen sources, and also a mixture of vitamins (Stanley, 1968) was used which allows growth of a broad spectrum of groundwater bacteria (Hirsch and Rades-Rohkohl, 1983). In portions (250 ml) of a 1:4 diluted sterile medium 250 ml of groundwater was added, and the cultures were incubated for 12 days on a rotary shaker (ca. 100 rpm) at 10°C. After incubation the microbial biomass was separated from the liquid by centrifugation, and freeze dried. Analyses made by courtesy of the Hygiene Institute of the Technical University Berlin (Germany) indicated the presence of *Arthrobacter, Pseudomonas, Flavobacterium*, and *Alcaligenes* species as components of the enriched microbial biomass. For the individual tests fresh PYGV medium in test tubes (4 ml; dilution 1:8) was inoculated with a small portion of the biomass, and the cultures were incubated on a rotary shaker for 7 days at 10°C. Afterwards, the cell density of microbial cultures was adjusted to an extinction value of 0.01 at 650 nm, and the incubation of five parallel cultures with chemicals added was continued for 24 h (1 day). In some experiments, the groundwater microorganisms were exposed to selected chemicals for 6 weeks (42 days). In this case a PYGV medium (1:100) was inoculated with groundwater (25 ml) without any pretreatment, and stationary cultures were incubated in triplicate at 10°C in the dark. The microbial biomass was estimated as ATP (Adenosinetriphosphate) using a method of Stutz et al. (1986). A Lumac Inc. NRB reagent was used for the ATP extraction, and a Lumac/3M Biocounter M 2010 for the ATP concentration measurements. A method by Liu (1981) was used for the colorimetric estimation of the dehydrogenase activity. Microbial respiration (uptake of oxygen) was measured by a L2-Method according to German Standard Methods of Water Testing (DEV, 1966). Results of all analyses were evaluated statistically using a "t-Test". For all data presented in the respective tables a value $p \leq 0.05$ was obtained. Minimum Effect Concentrations, i.e., MEC (1 day) or MEC (42 days) values, reflect 50% inhibition (EC_{50}) obtained in the most sensitive test and caused by individual chemicals. Usually, ATP measurement, and dehydrogenase activity were most sensitive tests.

Non-halogenated aromatics are relative less stable in the subsurface but accidentally, they appear in elevated concentrations in groundwater; for some of them a cancerogenic potential is well known (Schleyer and Kerndorff, 1992). Table 4 shows MEC values for the respective compounds.

A decrease in toxicity was sometimes related to increasing water solubility of the individual compounds. Ortho-xylene, e.g. inhibited groundwater bacteria at a concentration of 110 ppm while toluene did not show effect. A high concentration of benzene was tolerated in both short-term and long-term tests. Correspondingly, based on modeling the fate and transport of similar compounds (BTEX), Battermann and Meier-Löhr (2000) concluded that a monitored natural attenuation should be considered as a reliable remediation action for containment of a BTEX-plume in the subsurface. Basically, chlorinated but nitrated aromatics such as monochlorobenzene, o- or p-dichlorobenzene, 1,2,3-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene, could be degraded by natural consortia of groundwater microorganisms (Riis et al., 2000). In our experiments, nitrotoluene, and especially nitrobenzene showed toxic effects on microbial biomass and dehydrogenase activity already at low concentrations, while for similar effects with chlorinated aromatics concentrations near to full degree of saturation should be used (Table 5).

TABLE 4. Effects of non-halogenated aromatics on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 day)	MEC (42 days)
Benzene	1,770	1,100[a*]	1,000
Toluene	470	n.e.	290
o-Xylene	175	110[a*]	100
m-Xylene	130	81[a*]	
p-Xylene	200	n.e.	
1,3,5-Trimethylbenzene	20	n.e.	
Styrene	280	170[a*]	
Ethylbenzene	140	88[a,b*]	
Isopropylbenzene	50	31[a*]	

[a] Value obtained in ATP test; [b] Value obtained in dehydrogenase test; n.e. = No effect;

[*] Saturated solution.

In our previous experiments, different groups of soil microorganisms, and their respective enzymatic activities also resisted to high concentrations of trichloroethylene, tetrachloroethylene, and dichloromethane (Kanazawa and Filip, 1986, 1987).

Biodegradation of aliphatic halogenated hydrocarbons usually requires dechlorination under anaerobic conditions which is followed by an oxidative destruction of the residual metabolites. Indications exist that natural attenuation in aerated aquifers is not sufficiently effective to prevent these pollutants from spreading in the subsurface (Holmes et al., 1998; Bosma et al., 1998).

Polycyclic aromatic hydrocarbons (PAHs) represent an important group of hydrophobic organic contaminants especially in industrially polluted soils but because of their low water solubility and hydrogeochemical mobility they do not play important role as groundwater contaminants (Schleyer and Kerndorff, 1992; MacLeod and Semple, 2000). In our experiments saturated solutions of anthracene, fluoranthene and phenanthrene did not affect the biomass, i.e., ATP

TABLE 5. Effects of chlorinated or nitrated aromatics on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 day)	MEC (42 days)
Chlorobenzene	500	$310^{a,b*}$	300
1,2-Dichlorobenzene	100	62^{a*}	62
1,3-Dichlorobenzene	120	$77^{a,b*}$	
1,4-Dichlorobenzene	49	n.e.	
1,2,4-Trichlorobenzene	36	3^{b}	
Hexachlorobenzene	0.006	0.0038^{b*}	n.e.
2-Chlorotoluene	47	n.e.	
2,4-Dichlorotoluene	<100	$3^{a,b}$	
Nitrobenzene	1,900	10^{b}	10
3-Nitrotoluene	500	30^{a}	<100

For symbols see Table 4.

TABLE 6. Effects of chlorinated aliphatic hydrocarbons on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 day)	MEC (42 days)
Dichloromethane	16,000	$3{,}000^{a}$	
Trichloromethane	9,000	300^{a}	1,000
Tetrachloromethane	800	$500^{a,b*}$	
1,1,1-Trichloroethane	500	310^{a*}	
1,1,2-Trichlorotrifluoroethane	170	n.e.	n.e.
1,2-trans-Dichloroethene	600	$370^{a,b*}$	n.e.
Trichloroethene	1,100	300^{a}	300
Tetrachloroethene	150	$94^{a,b*}$	94
1,2-Dichloropropane	2,700	$1{,}700^{a*}$	
1,3-Dichloropropene	2,700	100^{a}	100
Hexachlorobutadien	2	1^{b}	
α-Hexachlorocyclohexane	1.	n.e.	
β-Hexachlorocyclohexane	0.24	0.15^{b*}	
γ-Hexachlorocyclohexane	1.9	n.e.	

For symbols see Table 4.

concentration of groundwater microorganisms, and the activity of dehydrogenase was slightly decreased only in samples contaminated with anthracene. Thus, it was redundant to present individual experimental results in Table 6. In soil samples contaminated with PAHs and heavy metals (Me), Maliszewska-Kordybach and Smreczak (2000) established a significant decrease of dehydrogenase activity in the order: control > PAHs > Me > PAHsMe.

Data in Table 7 show that some anilines exerted toxic effects on groundwater microorganisms already by concentration as low as 1% of a full saturation. Even more, trichlorophenol and pentachlorophenol exhibited in a short-term test the strongest toxicity of all chemicals under testing. However, results obtained in long-term test (42 days) indicate that in course of time, adaptation of microorganisms to elevated concentration of phenols may occur. Safronov et al. (2000) were able to enrich a microbial assemblage from wastewater that could be adapted to 2–3 g l^{-1} of phenol.

TABLE 7. Effects of anilines and phenols on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 day)	MEC (42 days)
N-Methylanline	30,000	300[a]	<30
N,N-Dimethylaniline	1,000	620[a,b*]	620
2,4-Dimethylaniline	1,000	100[a,b]	
Phenol	82,000	30[a]	
2,4-Dichlorophenol	4,500	10[b]	
2,4,5-Trichlorophenol	2,000	0.3[a]	>3
Pentachlorophenol	2,000	0.3[b]	3

For symbols see Table 4.

From other chemicals under testing, a high concentration of acetone (10%) was needed to obtain a strong decrease in biomass and dehydrogenase activity. Different pesticides inhibited groundwater microorganisms only at concentrations near to a full saturation (Table 8).

Using a respiratory test five chemicals that have been recognized as common groundwater contaminants by Milde and Kerndorff (1987) were also tested in mixtures for possible effect on groundwater microorganisms. The following concentrations were used: **Dichloromethane 660 ppm; Trichloromethane 300 ppm; Tetrachloromethane 30 ppm; Tetrachloroethene 5ppm; 1,2,4-Trichlorobenzene 1.3 ppm. No significant inhibition of the microbial respiration activity was observed in these experiments.**

In the absence of acute environmental risk, natural attenuation might represent a cost-effective alternative for the bioremediation of contaminated groundwater aquifers. However, this type of remediation strategy requires the identification and quantification of different natural mechanisms and limits. Hollender et al. (2000) performed microcosm studies, and in inhibition tests they used *Daphnia magna* which, however, may not represent groundwater organisms. In our experiments a mixed population of autochthonous groundwater microorganisms was used and our experimental conditions such as nutrient level and temperature corresponded with those usually existing in the subsurface. Yet, we applied chemicals in higher concentrations than those usually found in contaminated groundwater aquifers (Milde and Kerndorff, 1987; Schleyer and Kerndorff, 1992), i.e., a worst case situation was simulated in our experiments. In spite of this circumstance, groundwater microorganisms demonstrated a high degree of resistance against majority of the chemicals under testing. Even the most effective chemicals such as chlorophenols, nitrated aromatic hydrocarbons, and anilines had to be used in high concentrations in order to achieve significant inhibition of groundwater related microorganisms and their activities.

TABLE 8. Effects of some other chemicals on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 day)	MEC (42 days)
Acetone	Miscible	10,000[a]	
Atrazine	30	n.e.	
2-Ethyl-1-hexanole	1,000	620[a,b]	620
Ethyl-parathione	2.4	n.e.	
Thiophene	3,600	1,000[b]	

For symbols see Table 1.

4. Conclusions

Because the entire biosphere strongly depends on the biologically based processes of matter and energy transformation in the soil environment, there is a need for methods capable of testing and evaluating soil quality. The results discussed here emphasize the importance of process-related microbiological and biochemical parameters in this respect. The data obtained have to be weighted also with respect to physico-chemical soil characteristics which usually oscillate during the year seasons. A research need still exists as to the limit values which should tolerate acceptable risk but not overcharge the natural soil resiliency.

As concerns contaminated groundwater, its natural attenuation depends on different environmental factors, but especially on the resistance of the microbial population inhabiting the aquifer. Thus, a comprehensive examination of the microbiological, chemical, physical and hydrogeological conditions on site should be made before making final decision for applying or not of this type of remediation. Our results indicate that mainly, even high concentration of different chemicals do not inactivate microorganisms in groundwater samples, and thus upon conditions, natural attenuation to control and eventually remediate chemically contaminated groundwater aquifers might represent an alternative to other technologies.

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ENVIRONMENTAL EPIDEMIOLOGY AS A METHOD FOR RISK ASSESSMENT OF CHEMICAL POLLUTION

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Abstract. Environmental epidemiology studies are important tools in chemical risk assessment. There is a need for well-designed epidemiological large-scale study at international basis. The purpose of the risk characterization is to determine the need for action to aid regulatory agencies in risk management (justification for regulatory measure, acceptance of negligible risk, acceptable risk), as well as to inform the population for self-protection. The importance of epidemiological studies for risk characterization to prenatal exposure is important step in the hazard characterisation. Evaluation of health risk and offspring development has priority in the process of environmental chemical pollution risk assessment.

Keywords: chemical exposure, epidemiological studies, pesticides, metals, environment, water, air, soil

1. Introduction

Environmental epidemiology studies are important tools in chemical risk assessment.

The importance of epidemiological studies for risk characterization to prenatal exposure is important step in the hazard characterisation. Evaluation of health risk and offspring development has priority in the process of environmental chemical pollution risk assessment.

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2. Hazard Identification

In order to improve checking of chemical substances released into the environment, including the water compartment it is necessary to develop, along with the present conventional monitoring methods focusing mainly on the atmosphere, water and soil, new approaches enriched with monitoring of the overall flows of chemicals into and through the environment and monitoring of pollutants also in biological materials and wastes from the technosphere. Having in mind the precautionary principle the integrated assessment of the impacts on health and the environment should cover the complete life cycle of the products, with respect to significant properties of chemical substances such as the ability to accumulate in living tissues or resistance to decomposition and long life in the environment, characteristic for persistent environmental pollutants, in order to provide a solid base for risk assessment and standard setting (Simeonov, 2001; Bencko 2003; Bencko et al., 2004; Shore and Sander 2004).

2.1. HAZARD IDENTIFICATION AS A FIRST STEP OF RISK ASSESSMENT COVERS

Methods for analyses
Physical and chemical properties and routes and patterns of exposure
Metabolic and pharmacokinetic properties

2.2. THE SECOND STEP COVERS THE PRINCIPAL POLLUTANTS FOR DIFFERENT ENVIRONMENTAL MEDIA

2.2.1. *Industrial Pollution*

Chemical production plants are principal sources of environmental pollution. Chemical Industry produces acids, alkalis, salts, petrochemicals, synthetic fibers, plastics, pharmaceutical products fertilizers, paints, pesticides and many others.

Metallurgical plants in Bulgaria are important metal pollutants for soil, air, and water with, arsenic lead, cooper, cadmium, etc.

Pollution with specific organic substances, e.g. polyhalogenated and polycyclic aromatic hydrocarbons and locally by heavy metals namely mercury, cadmium and lead still remains a problem for environmental quality in most of the countries.

Transport and thermoelectric power station are responsible for air pollution by lead, sulfur dioxide, PAH.

2.2.2. *Water Pollution*

Water is essential to life, and the maintenance of an adequate supply of unpolluted water and especially safe drinking water is an essential requirement for both human health and good environmental quality. Human demands upon the earth's water are great. Water is taken for human use, irrigation and industry and is returned to environment as industrial discharge, agricultural run-off.

A subject of emerging interests is potential health risks due to presence of organochlorines in chlorinated drinking water. Chlorination may produce quite different profiles of chemical by-products in different areas, including carcinogens.

Also water from most individual wells, unfortunately, does not meet the standards for drinking water, especially in terms of nitrates.

Water quality is influenced especially by point sources of pollution (towns, villages, industrial and agricultural estates) and area sources (agriculture, erosion, atmospheric deposition). With decreasing pollution from point sources, the area sources are gaining importance, because in the last 2 years the amount of fertilisers used is going up again, especially in case of nitrogen fertilisers.

The investigation of possible risks for cancer from consuming chlorinated drinking water in human populations is difficult.

2.2.3. *Other Sources*

Agriculture
Household products
Food
Medicaments
Transport fuel

2.3. EXPERIMENTAL AND HUMAN DATA FOR ADVERSE EFFECT AND RESPONSE

Adverse effects in animal studies-validity and importance of experimental data
Dose response quantitative relationship between the dose and answer
Dose effect relationship between different effects and dose qualitative relationship
Exposed population

2.4. ROUTES OF ENTRY

Exposure time and levels
Exposure assessment

Exposure assessment should answer the following questions for the substance under study: are potential parents exposed; what is the route of exposure (breathing, drinking water, dermal contact, other, combine quantity, frequency, duration.

Exposure is assessed using monitoring data, using modeling for estimating concentrations.

3. The Data and Information Needed to Fully Assess Exposure is not Available

There are many *Tools* and *Models* for exposure assessment. Specialized Priority setting tools are effective in comparing multiple chemicals rank concerns broadly and are not intended to provide accurate assessments. They are used to rank and compare large number of chemicals of the standardized criteria for different purposes.

Screening level tools are used in the absence of appropriate monitoring data in screening level assessment or to prioritize chemicals for future work.

Assumptions and default values are used to fill these data gaps. In case of parent exposures these gaps are usual practice.

Only these partial enumerations of some existing models demonstrate that they can not help much the cancer in o offspring danger of the environmental chemical pollutants.

Risk assessment is the use of factual database to define the health effects of exposure of individuals or population to environmental chemical pollutants.

4. Risk Characterization

Relationship using real exposure data and effect/answer/using experimental and epidemiological study results is the step for risk characterization.

Research priority should be placed upon improving methods for exposure assessment and into development of innovative epidemiological methodologies for study design and analyses. Better epidemiological tools and improved quantification to design epidemiological studies, to trace pathways for effects in offsprings are needed.

4.1. THE IMPORTANCE OF EPIDEMIOLOGICAL STUDIES FOR RISK CHARACTERIZATION RELATED TO PRENATAL EXPOSURE

Cancer of offsprings should be regarded as one of the most dangerous potential outcome of the environmental chemical exposure.

There is a need for well-designed epidemiological large-scale study at international basis for the evaluation of health risk and offspring cancer development.

The purpose of the risk characterization is to determine the need for action to aid regulatory agencies in risk management (justification for regulatory measure, acceptance of negligible risk, acceptable risk), as well as to inform the population for self-protection.

5. International Documents

(UNEP 1997; Montreal Protocol 1999; EHC 214, 2000; Kaloyanova 2007) The World Health Organization, UNEP IARC and others organizations have long lasting experience for preparation of information documents evaluated at different levels.

- Screening Information Data Set (SIDS) for the substances with limited toxicological data
- International Chemical Safety Cards (ICSC)
- Concise International Chemical Assessment Documents (CICAD’s)
- Environmental Health Criteria Documents (EHC)

6. Legislation measures (Annual Bulletin 2001)

7. Training and Public Wariness Rising

Workers training is regulated in almost all developed countries with special curricula and repeated periodically, to include the new technologies.

8. Conclusions

Environmental epidemiology in combination with other methods for risk assessment of environmental chemical pollution need more attention at iternational level. These kind of studies should have priority and encouragement in collaboration between NATO and partner countries.

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THE USE OF BIOMARKERS IN THE TOXICOLOGICAL RISK ASSESSMENT

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Abstract. The risk assessment procedure made either for protection of ecosystem or human health is normally based on standardized toxicological test methods. Most of these tests are expensive and require in vivo animal experiments. On the other side, it is important to detect low concentrations of toxic substances in various mixtures that are present together with other non-toxic compounds, as early, as possible. For this early warning the traditional methods in toxicology cannot supply an adequate basis. Recently, some relatively inexpensive and simple methods suitable for classification of dangerous wastes and pollution of surface water have been developed. The practical implementation of such methods would have of high significance in the assessment of the state of surface waters (rivers and lakes), as well, as industrial effluents. In order to compare the performance of the various bioassays a series of examinations have been carried out with various methods. Microbio-test kits seem to be especially useful for the water quality assessment of rivers and lakes. Data are given on the monitoring of some important habitats in Hungary. The toxicity estimation with different bioindicators discussed in the presentation can give us a habitat-specific indication of the pollution. The results revealed that the alternative tests are sensitive to indicate the combined effect of various pollutants in aquatic ecosystems. It seems to be that the tests using crustacean species would give realistic results in well-defined point sources, but they can be accepted somewhat more sceptic when comparing samples taken form different habitats. *Daphnia* heart rate were specific for a number of compounds. Presently the luminescent bacterial systems are extensively used as standardized bioassays in the environmental impact assessment. An important conclusion of the results that there is no universal bioassay available for detection of all types of pollution. The best results can be obtained with employment of a battery of bioassays.

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Keywords: bioindicators, bioassay, risk assessment, microbiotests

1. Introduction

The process of environmental impact assessment involves the major elements of identification, measurement, interpretation and communication of impact. Traditionally, environmental risk has been assessed by chemical residue determination in samples from the affected site. This approach has several limitations. The most important factor is the availability of the chemicals from the environmental compartments to the biological receptors, defined as bioavailability (Kiss et al., 2002). On the other side, during the analysis of environmental risk ecological impact on whole ecosystems should be assessed. It requires a complex testing scheme where the sensitivity of different species to different contaminants usually vary. The risk assessment procedure made either for protection of ecosystem or human health is normally based on standardized toxicological test methods. Most of these tests are expensive and require *in vivo* animal experiments. In a number of cases, it is important to detect low concentrations of toxic substances in various mixtures that are present together with other non-toxic compounds, as early, as possible. For this early warning the traditional methods in toxicology cannot supply an adequate basis.

2. Bioindicators

Bioindicators for the assessment of the environmental quality are required by EU legislation (Water Framework Directive) – in order to define the GOOD ECOLOGICAL STATE specified as allowing only a slight departure from the biological community which would be expected in conditions of minimal anthropogenic impact. A set of procedures for identifying that point for a given body of water, and establishing particular chemical or hydromorphological standards to achieve it, is provided. Biological quality can be assessed by different organisms, e.g. algae, aquatic vegetation, invertebrates and fishes.

What is a bioindicator? Bioindicators are organisms that contain qualitative information on the quality/health of the environment or ecosystem (Markert et al., 2003). They can be any biological species or group of species whose function, population or status can used to determine environmental or ecosystem integrity (Mccarty et al., 2002). Bioindicator organisms can deliver information on alterations in the environment in the form of physiological, chemical or behavioral changes.Various species are sensitive to different chemicals, at various degree. The indicator species are highly sensitive to some specific chemicals, depending of the environmental cc. of the given chemicals (Moriarty, 1990; Lopez-Barera, 1995).

The first question: are bioindicators alternatives to chemical environmental quality criteria. Some of the authors have answered yes. They created the term: alternative test methods (Fentem et al., 2003). However, in fact the bioindication tests are not alternatives to the standardized toxicological and chemical methods, but they rather have a different role in environmental risk assessment. Let us explain this thesis on aquatic ecosystems, since these systems are among the most productive and diverse habitats. Aquatic plants and animals are exposed to the effects of various stressors. These communities reflect changes in conditions over time to these effects. Biological assessments provide direct measures of cumulative response of the biological community to all sources of stress.

Biotic index is used to monitor the sensitivity of taxa to pollution. Various biotic indices are available. Organisms are assigned tolerance values which range from 0 to 10, depending on the organism's sensitivity to changes in water quality and habitat (tolerance values increase as water quality decreases). The biotic index was originally designed for use at species level, but it is frequently used at the family level.

According to the WFD the UK has carried out a multisite study in the STAR project (Buffagni et al., 2004). In general terms, it was established firstly to define assessment systems able to evaluate general degradation and classify European river sites and secondly develop impact-specific modules (e.g. set of metrics): some of them will be tested during the STAR activities. For example, although all organism groups are affected by acidification, benthic diatoms and/or invertebrates may be considered as the best indicators.

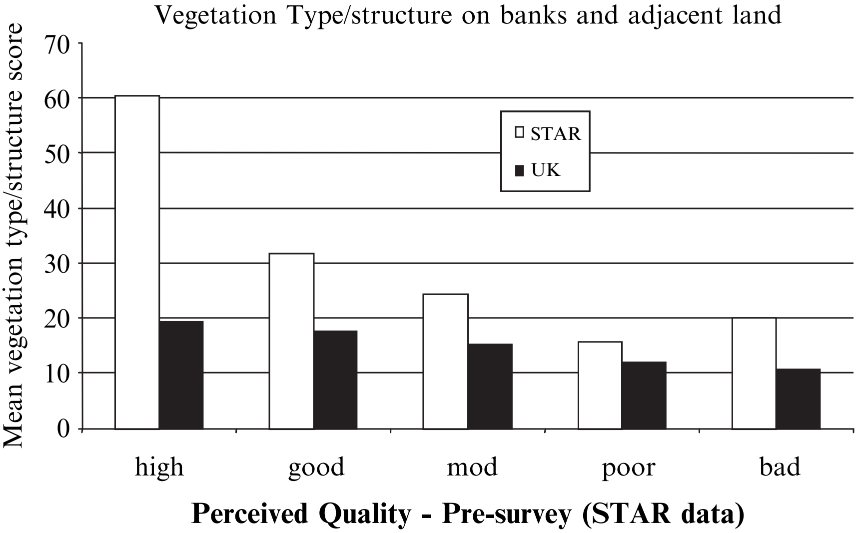

Figure 1. Comparison of average scores for ecological state between UK and rest of the countries involved in the STAR project.

It has been concluded that it is really possible to make the results of the biological classification systems comparable across Europe. Based on the pilot exercises performed within a number of Geographic Inter-calibration Groups and the STAR Project, it seems realistic to compare the data and classification results of different countries and stream types, provided that there is agreement on how to derive reference conditions.

If enough data is available, the main constraints are linked to the discussion and agreement phases of common protocols and procedures. The assessment methods are still under development (e.g. fishes, macrophytes). However, there were a difference among various countries in their practices and standards.In Figure 1 it is shown that in this respect, in case of vegetation type/ structure the high ecological state seemed to be the most problematic.

High scores indicate high quality; lower scores show increasing departure from naturalness.

Daphnia magna (Figure 2) is a standard organism to use in bioassays because it is sensitive to changes in water chemistry and is simple and inexpensive to raise in laboratory (Kuehn et al., 1989). It seems to be that the toxicological studies with Daphnia would give realistic result in the case a well defined point sources, but they can be accepted with somewhat more sceptic way when comparing samples taken from different sources.

It is common to conduct bioassays using endpoints other than death, e.g. the heart rate of Daphnia (Kiss, 2001) is measured under microscope.

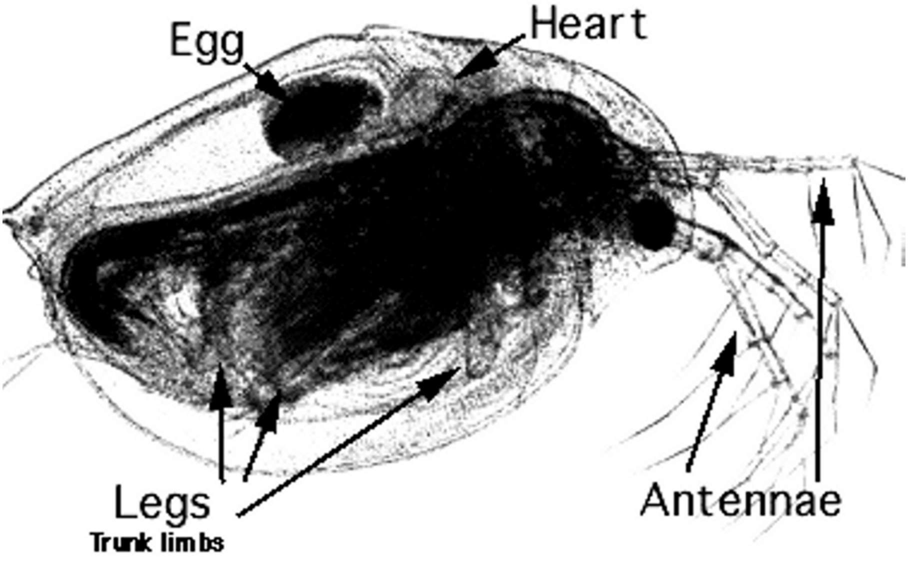

Figure 2. Microscopic picture of *Daphnia magna*.

Principle of the method: Place one Daphnia with a drop of the standard solutions to a microscope slide. Record the heart rate of the control animals under dissecting microcope. Repeat the measurement at 30 min, 60 min, and 90 min. The same observation should be made at each concentration of the test material. 5–5 replicates should be made both at the control and at each concentration level. The observed heart rates are plotted into a graph against time to draw a regression line. The slope of the control line is calculated, as well as of those obtained at the various test concentrations. If there is a significant change of the slope, it indicates a toxic effect.

As to the heart rate, it seems to be more specific only to a limited number of compounds. However, in case of an effect, it is one of the most powerful test methods. We found nice dose-response functions for pyrethroid type pesticides. Figure 3 shows one of these results for deltametrine in the 0.025–1.25 mg/l dose range.

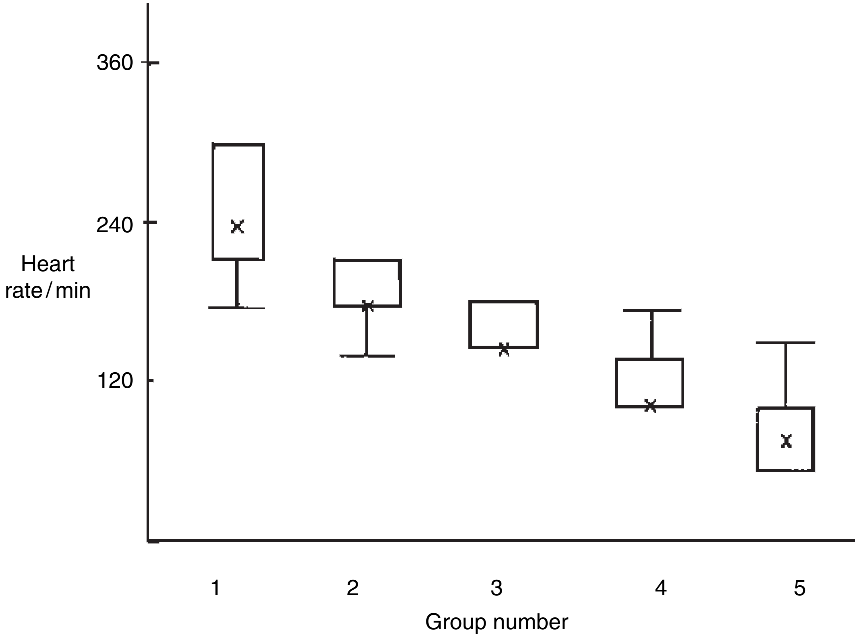

Figure 3. Decrease of *Daphnia magna* heart rate caused by deltametrin. Concentrations in mg/l: 1 – 1.25, 2 – 0.5, 3 – 0.1, 4 – 0.05, 5 – 0.025.

Some relatively inexpensive and simple methods suitable for classification of the pollution of surface water have been developed (Persoon and Jansen, 1998; Persoon, 2000). Microbiotests (or toxkits) the test organisms are provided in a dormant form. As in this way the difficult and labour-consuming task of culturing can be avoided, such tests can be conducted in a relatively simple laboratory (e.g. in an industrial firm). In extreme cases, some microbiotests can be conducted even in the field.

The most widely used are:

- Algaltoxkit with Selenastrum capricornutum
- Charatox with Nitellopsis obtusa
- Thamnotoxkit with Thamnocephalus platyurus
- Daphtoxkit with Daphnia magna
- Protoxkit with Tetrahymena thermophila
- Microtox with Vibrio fischeri

We used the Thamnotox kit extensively, which is suitable for demonstration of the principle of these methods.

The Thamnocephalus toxicity test-kit contains all the materials to perform standardized, simple and cost-effective bioassays for screening toxicity in freshwater. Using Instar II-III larvae of the fairy scrimp *Thamnocephalus platyurus* (Figure 4) hatched from cysts (dormant eggs), an acute toxicity test is executed in 24 h in a multiwell test plate. After 24 h, the dead larvae in each test well are counted and the % mortality calculated.

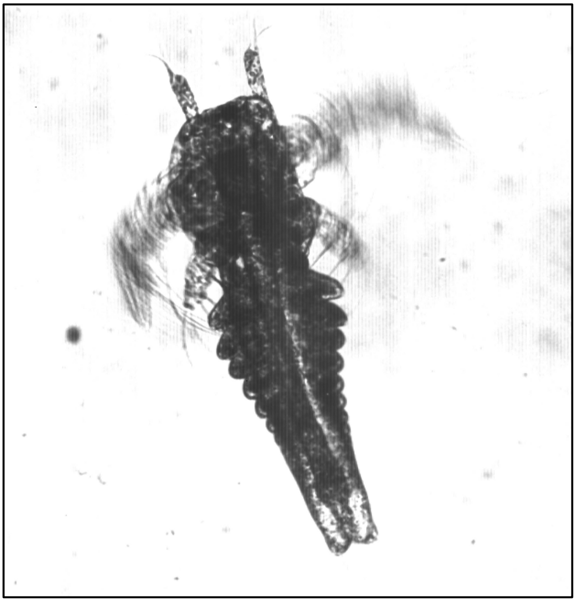

Figure 4. Star-III larvae of the fairy scrimp *Thamnocephalus platyurus*.

For some mixtures of pollutants there was a correlation between Thamnotox and Daphnia heart data. It has been observed earlier in the Veszprém Séd (in the year 2000), probably caused by an illegal discharge of municipal waste (Kiss, 2001).

Thamnocephalus test can differentiate among substances showing a kind of selectivity if there are great differences in the concentrations of the various components. Nevertheless, Thamnocephalus test show real specificity to some substances (cyanides, fluorides etc.).

If an aqueous solution there are a number of pollutants of relativity high concentration each, Thamnocephalus test may not be suitable for indication.

For detection of high concentration of Na in the soil Thamnocephalus test is preferable to use. The adverse effect of sodium to natural ecosystem may be exerted in the surface layers of the soil, especially because it can be found usually as NaCl salt. Similarly, the Cd pollution in the soil may be preferably detected by Thamnocephalus test. It is well-known that Cd is hazardous not only with respect of the ecological systems, but also has a significant toxic effect to humans. The Cd substances are neurotoxic, carcinogenic and teratogenic, too.

In Hungary, the practical implementation of such methods would have of high significance in the assessment of the state of surface waters. In order to compare the toxicity detection of the various bioassays and some of the conventional Daphnia toxicity tests a series of tests have been performed with Thamnotox and Daphnotox kits. Based on the results of these studies and other data of OECD the Thamnotox kit has been standardised, as Hungarian Standard.

ToxAlert ®10 test was developed by Merck, and is the field version of the ToxAlert ®100 luminometer (BS EN ISO 11348.3, 1999). This test uses the bioluminescence inhibition of the marine bacterium *Vibrio fischeri* (Figure 5; Doherty, 2001; Galli et al., 1994). Bioluminescence is a rapid indicator of the metabolic status and of the viability of the cell. The enzyme involved in the process is bacterial luciferase. Chemicals or chemical mixtures, which are toxic to the bacteria, cause changes in some cellular structures or functions such as the electron transport system, cytoplasmic constituents or the cell membrane, resulting in a reduction in light output proportional to the strength of the toxin. The light output of luminescent microorganisms which emit light as a normal consequence of respiration is read by a luminometer.

At the beginning of the measurement firstly the test suspension is prepared, using freeze-dried bacteria and reconstitution solution. The luminescence intensity of the test suspension is measured in RLU (relative luminescence unit), then the control as well as the sample solutions are added to the test suspension. Luminescence intensity is measured again after the previously set exposure time, e.g. 30 min. The ToxAlert ®100 luminometer calculates the inhibition effect of the samples automatically in % values.

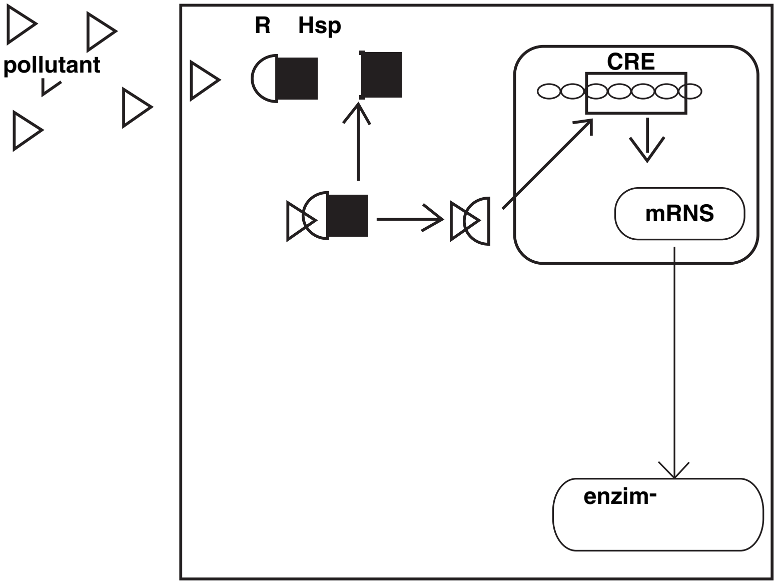

Figure 5. The mechanism of the effect of pollutants in a cellular system similar to *Vibrio.*

Let the toxic substance be a polyaromatic hydrogenic carbon (PAH), which is highly dangerous as carcinogenic and teratogenic material, even at low dose level. It is connected to an intracellular receptor (in case of PAH the receptor is called “AH”). This receptor is immobilized by a Hsp protein in normal state. After the effect of the toxic substance the receptor-substance complex can move freely to the appropriate region of DNA, and will affect the enzime expression.

Duckweed (*Lemna minor*) is a relatively new bioindicator suggested by EPA (1996) and OECD experts (OECD, 2002). The objective of this toxicity test is to quantify substance-related effects on vegetative growth (Wang, 1990). The main advantages: *L. minor* is a species easy to collect and culture in laboratory, and can give rapid test results.

Two types of Lemna populations can be used:

(a) Standard laboratory cultures. They are cultured in sterile conditions and suitable for test procedures for regulatory purpose.
(b) Strains collected in a natural habitat, not necesserily cultured in sterile medium. They may be used for a habitat-specific indication of the toxic pollution.

Culture period: 8 weeks prior to use. One control culture and different concentrations of the test substance are applied. The test concentrations should be prepared by dilution of a stock solution having been prepared by dissolving the test substance in the test medium.

The experiments are performed in triplicate, each test vessel inoculated with ten fronds of Lemna. The test is terminated 7 days after the plants were inoculated into the test vessels. Frond numbers and the appearance of the colonies should be recorded at the beginning, then at 72, 120 h and at the termination of the study.

"Average specific growth rate" (μ) is calculated on the basis of changes in frond number in controls and each treatment group. Changes in the biomass are also detected at the same occasions as the frond numbers. This is calculated on the basis of changes in dry weight, fresh weight or total fron area.

The value of LC_{50} are calculated on the basis of $\%I_r$ with linear regression (following log transformation of concentration data), and graphical method. Percentage average growth rate (%Ir) is calculated as follows:

$$\%Ir = (C\mu - T\mu) * 100/C\mu$$

where:

$C\mu$ is the growth rate in the control

$T\mu$ is the growth rate in the test group.

In our examinations Lemna minor showed the most controversy results. At some sites of the river Tisza growth stimulation could be detected instead of growth inhibition. The possible reason of this behaviour of Lemna minor has been investigated. According to the results the doubling time (T_D) shows a strict correlation with the original environmental conditions of the test system. Various types of environment have been included in our tests: instable environment characterized as low N and higher P content of water; favourable environment with optimal essential nutrient factors. Populations living originally in the first environment will show lower relative growth rate, as a final result of nutrient availability. They are more vulnerable to toxic chemicals. In other experiments (Szalay et al., 2000; Kiss et al., 2001) it has been shown that there is a nutrient optimum for Lemna minor. Either low or excess N is not favourable for the duckweed.

In order to study the performance of the various alternative tests a comparative study has been carried out with different samples collected from different environmental compartments (soil, surface water and ground water, etc.) and from various geographical regions.

Investigations involved lake Balaton and its catchment area and inflows. Figure 6 shows Thamnocephalus mortality results at different sampling sites of lake Balaton (samples were taken in the year 2000). The differences are seen well.

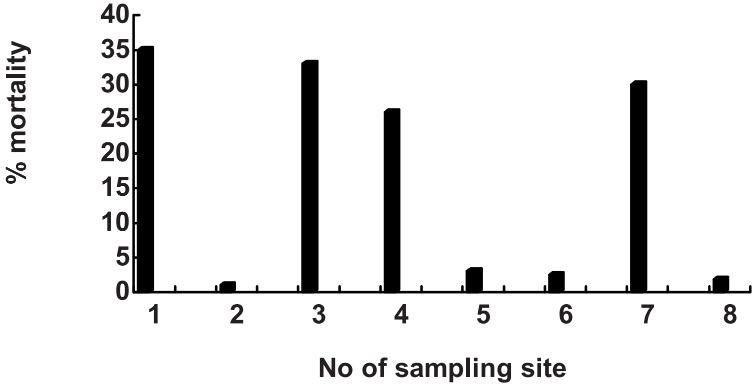

Figure 6. Thamnocephalus mortality results at different sampling sites of lake Balaton.

In the river tests (Tisza and Danube) the mortality rate in Thamnotox test was between 5% and 40%. The latter, relatively high value was detected in the most industrialized sites with a number of waste water discharges. Here the differences among the various tests maybe caused by the selective toxicity of some compounds, mainly pesticides, heavy metals, etc.

When testing soil samples, the *Thamnocephalus test* showed excellent consistency with most contaminants but was oversensitive in the case of groundwater samples. The *Vibrio fischeri* bioluminescence inhibition test (ToxAlert) behaved in a different way, reflecting well the distribution of most contaminants in groundwater samples.

It is well-known that the biological systems have a filtering function, therefore the same chemicals have different bioavailability for the various species and consequently they cannot express their nutritional or toxic function in the same degree. In this respect the bivalves (e.g. freshwater mussels) proved to be good bioindicators of many pollutants, especially heavy metals. They accumulate these toxic substances and one can detect the pollution by a follow up of the periodic activity of the animals.

3. Conclusions

It seems to be that the tests using crustacean species (also the cyst-based ones) would give realistic results in the case of well-defined point sources. These results models well an "early warning" situation, when an acute, sudden concentration increase occurs like in a specific point of river Tisza, or in some sites of Veszprém Séd.

In a special, small wetland where the distribution of the pollutants is quite irregular, both in the cross section of the site and against time, the Daphnia tests often showed *hyperpersensitivity to some pollutants*, while the average sensitivity proved to be much lower as compared to the Thamnotox test.

Sensitivity of used tests against $C_2Cr_2O_7$, the heart rate of Daphnia magna proved to be very sensitive method. It can be well explained by the fact, that having a heart frequency decrease is not neccesserily connected to the animal mortality, rather the toxicity are evaluated at sublelhal dose levels (Figure 7).

Toxalert is less sensitive, however it reacts to most of the soluble components of the groundwater in a selective way.

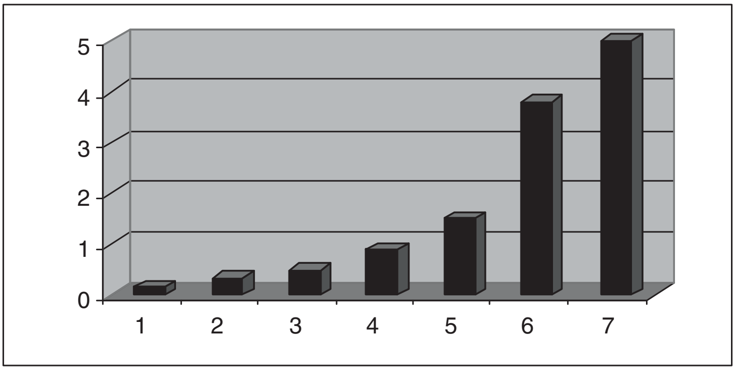

Figure 7. The sensitivity of some test methods. 1: Thamnotox; 2: Algatox; 3: Daphnia heart rate; 4: Daphtox (pulex); 5: Daphtox (magna); 6: *Lemna minor*; 7: Rotoxkit (*Brachionus calyciflorus*).

As a conclusion of the above facts, a combination of the individual tests can yield the best results (Cairns, 1983). For example using Toxalert the cyanide can be detected in the soil samples before reaching the ground-water. This is very important, because the cyanide is known as especially dangerous substance with a limit value of 1 mg/l or below for the underground waters.

The simultaneous employement of several types of test we used gave the best results (Cairns, 1983). According to the results a multispecies approach is suggested. On the other side the test methods will give us the possibility for a habitat-specific indication of the pollution. (Kiss, 2001; Kiss et al., 2003). In this respect the various indices of biodiversity may also be useful for environmental assessment.

In addition, it is important to mention that thamnotox kits work very well and they gave exact dose-response function in the detection of various cyanobacterial toxins like microcystin (Törökné and Takács, 2000). Consequently they can be applied to those sites like Balaton, where these algae play an important role.

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HUMIC SUBSTANCES AS NATURAL INTERACTING AGENTS: THEIR CHARACTERISTICS AND POSSIBLE FATE IN ENVIRONMENT

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> *The further you enter into it, the deeper it becomes.*
> Dante Alighiery

Abstract. In the last decades, structural complexity of humic substances and their role in natural environments have been widely discussed. Their persistence and/or susceptibility to biological decomposition, however, requires for further research. Here we present a contribution dealing in part with humic acids (HA) extracted by alkali from soils differing in metal contents, and which might represent naturally occurring organic-mineral-metal complexes. If exposed to microbial activities, and especially if easily utilizable carbon and nitrogen sources were not available, HA from soils containing elevate metal contents or from a soil site located near to a Mg-plant and heavily contaminated with this element, were found to support growth of soil microorganisms. At the same time, the structure of HA underwent several structural transformations. The FT-IR spectroscopic investigations indicated releases of metal and silicate constituents from the HA preparations.

Keywords: humic substances, microbial utilization, structural transformation

1. Introduction

Soil represents the largest reservoir of carbon in terrestrial ecosystems. The total pool of C in soils comprises 1,200–1,500 × 10^9 Mg C, i.e., about five times

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more than the carbon content in total vegetation on our planet Earth (Batjes, 1996; Breuer, 1999). Only a small part of C bound in the soil organic matter (SOM) comes from a recent plant detritus; 60–80% belong to humic substances. Körschens (2004) underlines the high importance of SOM not only for soil fertility but, especially for the environmental protection, particularly because a close relationships between the SOM and to the global cycles of carbon and nitrogen. There is no doubt that individual fractions of SOM may differ in their stability. Basically, Schulz (2004) recognizes an inert SOM pool, and a decomposable one. Because of their rather high molecular weight and polymeric structure, humic substances have been regularly regarded as highly resistant to biological and chemical degradation. This might apply especially for humic acid (HA) fraction, which consists different phenolic compounds of lignin and/or microbial origin, and is capable of forming complexes with soil mineral components (Haider et al., 1975; Filip and Alberts, 1993). Nevertheless, exceptions to the rule also exist as discussed, e.g. by Filip et al. (1998).

2. Structural Peculiarities of Humic Substances

In any matrix, the biodegradation of organic substances is regulated by structure of the substrate, quantity and distribution of its reactive sites, and furthermore it depends on the degradation activity of living cells, such as microorganisms (Anderson, 1990). HA consist of polymeric micelles, the basic structure of which is represented by aromatic rings of the di- or trihydroxy-phenol types, and bridged by $-O-$, $-CH_2-$, $-NH-$, $-N=$, $-S-$, or some other groups. They also contain several OH groups either free or bounded by double linkages of quinones (Stevenson, 1985). A simple hypothetical structure of HA containing reactive hydroxyl and carboxyl groups was published by Flaig (1960) and is shown in Figure 1.

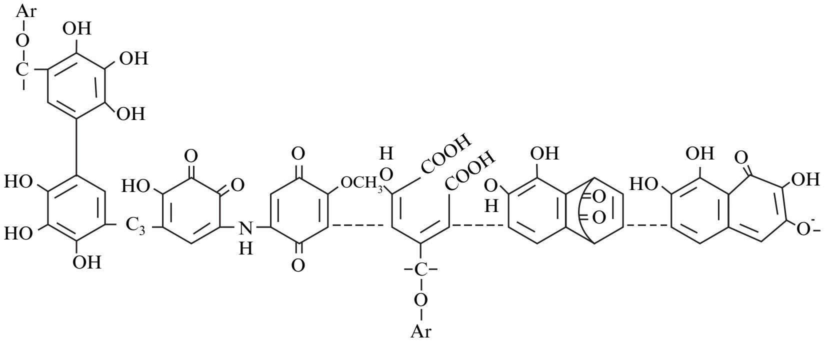


Figure 1. Hypothetical structure of soil humic acid according to Flaig (1960).

Several years later, Hatcher et al. (1989) used a cross-polarization and magic-angle spinning analytic technique, which enabled him to suggest a simple structural model of humic acids extracted from a paleosol and volcanic soil samples collected in Japan (Figure 2). The model is based on a highly resistant aromatic "core", but it consists also of several carboxyl groups, which should appear typical especially in HA formed under oxidative conditions.

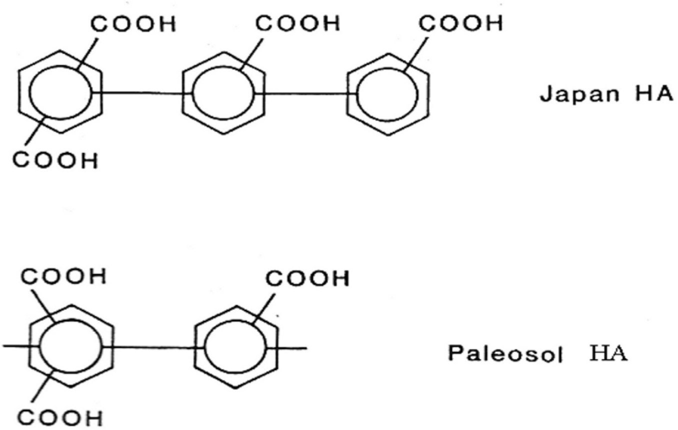


Figure 2. Humic acids core structures as proposed by Hatcher et al. (1989).

The existence of numerous aromatic nuclei containing both hydroxyl and carboxyl radicals have been documented by Haider et al. (1975) also for HA-like dark in color pigments formed under aerobic conditions in cultures of some soil microscopic fungi (Figure 3).

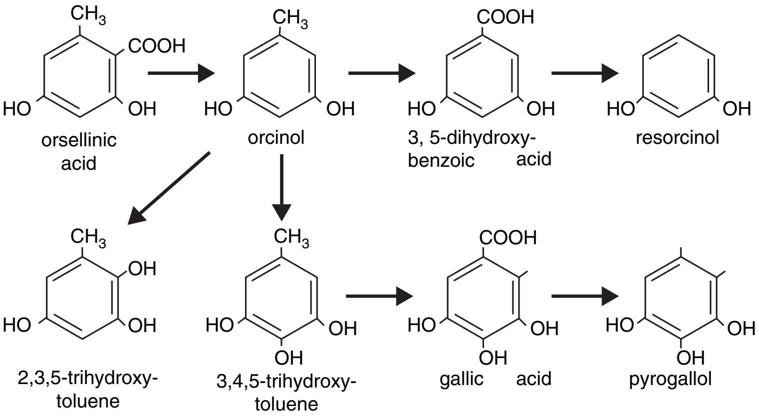


Figure 3. Precursors of humic acids synthesized by soil fungi. (Haider et al., 1975).

In difference to the HA structures based on aromatic rings, Filip and Alberts (1992) reported a strong aliphatic character for HA extracted from samples of soils and sediments collected from thermal sites in Island. The individual HA preparations were extremely high in their ash contents. They were also very rich in nitrogen and appeared strongly bound to mineral matrices, mainly silicates.

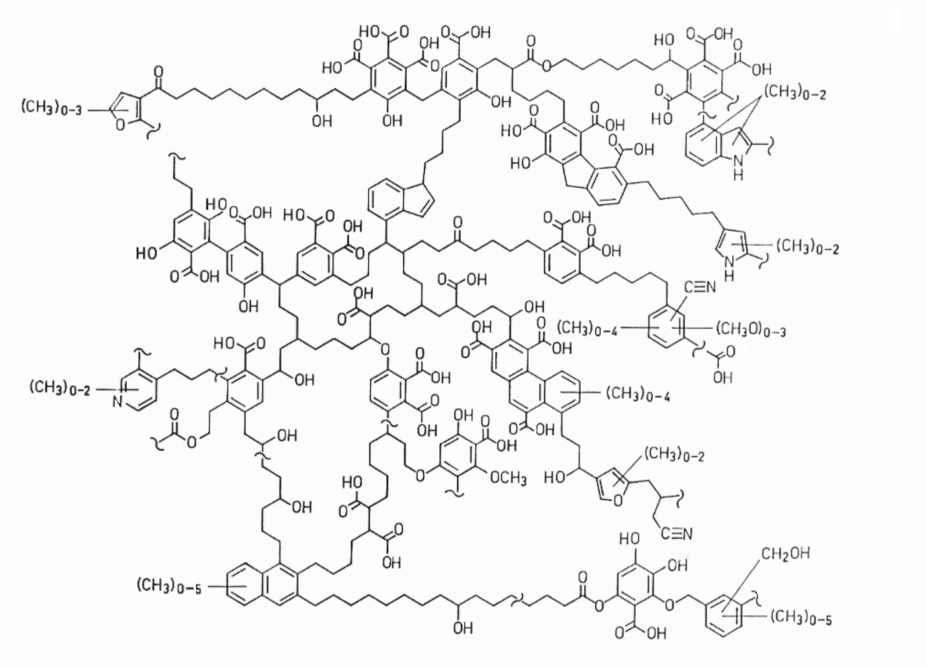


Figure 4. Complex structural concept for humic acids. (From Schulten, 1994.)

A complex carbon based structural network of HA as suggested by Schulten (1994) is shown in Figure 4. The author constructed this model in accordance with analytical data obtained by pyrolysis-gaschromatography/mass-spectrometry (Py-GC/MS), pyrolysis-field-ionisation mass-spectrometry (Py-FIMS), ^{13}C nuclear magnetic resonance (^{13}C NMR), and also after evaluation of a chemical oxidative and reductive degradation of different HA preparations. Basically, it consists of numerous chemically coupled aromatic nuclei, and different aliphatic chains. The same author pointed on a wide variety of aromatic isomers that might be coupled with aromatic nuclei in humic substances (Schulten, 1999). In a comprehensive review, Sutton and Sposito (2005) correspondingly designated HA as collections of diverse, relatively low molecular mass components forming dynamic associations, and stabilized mainly by hydrophobic interactions and hydrogen bonds. These rather new views on the structure of HA indirectly indicate that also a further need exists for the re-evaluation of biogeochemical pathways of HA formation, i.e. humification process itself. It seems rather misleading in this respect, however, to describe humification simply as biochemical weathering of plant and animal remnants, as proposed by Myneni et al. (1999). In such a view, synthesizing processes carried out by microorganisms, and evidently contributing to *de novo* formation of humic substances from simple organic substrates in different environments (Filip et al., 1972, 1976; Haider et al., 1975; Filip and Alberts, 1993; Filip and Claus, 2002), seem disregarded.

3. Natural Complexes of Humic Substances with Minerals and Metals

In soils and sediments humic substances naturally occur in different associations with inorganic components, especially with clay minerals and metals (Filip, 1968; Stevenson, 1985). Mechanisms of the respective binding actions are schematically shown in Figure 5. In our investigations, and using spectroscopic methods, we were able to demonstrate HA binding capacities in clay minerals such as kaolinite, illite and montmorillonite (Filip, 1968). From the results obtained we postulated that clay mineral lattices act as molecular sieves capable of binding low (with kaolinite) or higher condensed (with montmorillonite) molecular parts of HA preparations We could also demonstrate that depending on type of cations in exchange positions of a clay lattice, structural transformations of the adsorbed HA occur (Filip and Alberts, 1994).

Kerndorff and Schnitzer (1980) studied an efficiency of metal sorption on HA under different pH-conditions. At pH 5.8, e.g., the binding preference was as follows: Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn. A competition for the reactive sites in HA, mainly COOH or OH groups, was assumed as existing for some metal ions.

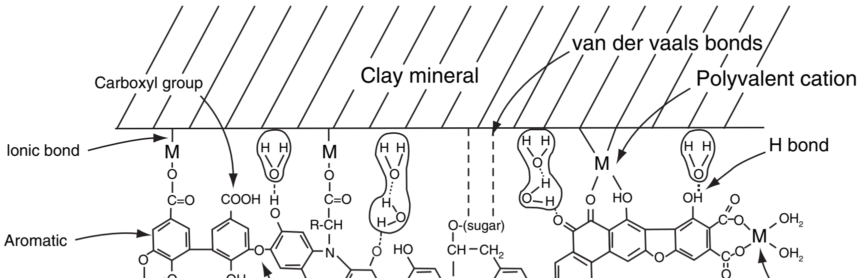


Figure 5. Links of model humic acid structures with metals and a clay surface. (From Stevenson 1985.)

In a comprehensive review, Senesi (1992) discussed different molecular and mechanistic aspects of complex formation between humic substances and metals, which occur in natural environments, and evaluated suitability of different methodical approaches in this field. Due to a complex nature of HA, infra-red (IR) spectroscopy has been find as useful. In the IR spectra, the appearance or disappearance of the absorption bands of particular functional groups such as CH, NH, OH, C═O, and C═C allows to identity the main sites of HA complexation. Also by using IR spectroscopy, Alberts et al. (1992) concluded that carboxylic structural units in HA play an important role in formation of complexes with Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} ions. In preparations of estuarine humic and fulvic acids, oxygen-, and nitrogen-containing functional groups have been found as binding of Cu^{2+} ions (Alberts and Filip, 1998). The copper binding capacity, however, was reduced by 30–40% in the presence of competitive trivalent metal cations such as Al^{3+}, and Fe^{3+}.

Undoubtedly, not only the chemical complexity of humic substances, but also their natural bindings with metals and clays affect their resistance or susceptibility to microbial degradation. In order to contribute to illumination of this field, we exposed HA preparations extracted from soils that differed either naturally or due to anthropogenic activities in their contents of metals to microbial activities in numerous laboratory experiments.

4. Microbial Utilization and Transformation of Humic Acids from Soils with Different Metal Contents

The HA preparations were isolated from samples of three Slovakian pseudogley soils located at (i) Senne – a soil under permanent pasture with a low metal content; (ii) Ilija – an arable soil which exhibited a slightly elevated metal content; (iii) Jelsava – an uncultivated soil site near to a metal processing plant, and exhibiting a highly elevated content of Mg. Analytical data of the individual soil samples are given in Table 1. In the further text, the soilsamples are designated as a “Control” (Senne), “Metal-Rich” (Ilija), and “Mg-Rich” (Jelsava).

The microbiological analyses of the individual soil samples resulted in average counts of bacteria (CFU) as presented in Table 2. In comparison to bacteria, the CFU numbers of microscopic fungi were lower by one order of magnitude in Control and Metal-Rich soils, and by two orders of magnitude in Mg-Rich soil, respectively (not shown in Table). After a 3 week incubation, the CFU numbers of bacteria increased up to three orders of magnitude in the individual cultures. Simultaneously, different microbial species could be identified by using a BIOLOG® system.

The HA preparations appeared to be differently utilizable by the soil microorganisms. When serving as a supplemental source of nutrient, i.e., in a full-strength nutrient broth, the degree of utilization after 21 days was 63%, 57%, and 44% for the HA from Control, Metal-Rich and Mg-Rich soils, respectively. As shown in Figure 6 for HA from Met-Soil, the microbial utilization was further enhanced when the humic preparations served as a sole source of C or N. In this case, the utilization degree reached up to 72% after 1 year (not shown in Figure 6).

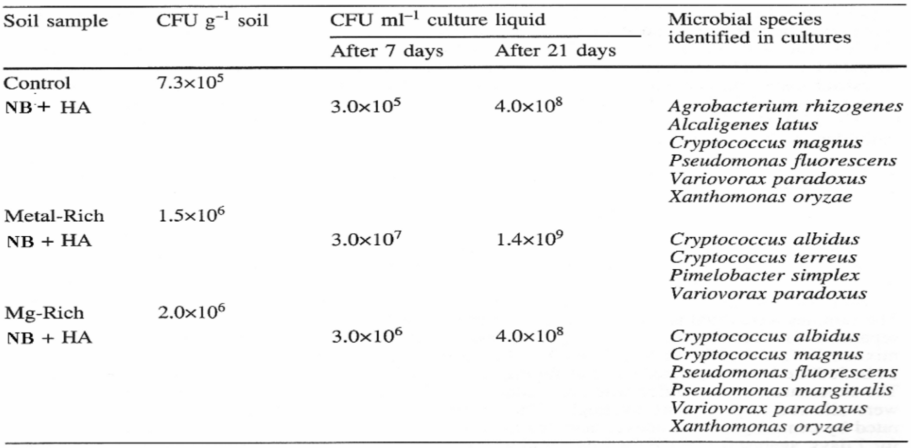
TABLE 1. Characteristics of soil samples.

Characteristics	Soil sample from		
	Site Senne	Site Ilija	Site Jelsava
General			
pH (H_2O)	7.8	6.6	9.0
C_{ox} (%)	1.2	2.5	1.1
N_{tot} (%)	0.14	0.28	0.14
Potentially toxic elements			
(mg kg^{-1} soil d.w., aqua regia)			
As	6.5	49.0	12.0
Cd	0.1	0.7	0.1
Cu	5.4	40.0	10.0
Hg	0.1	0.2	0.1
Mg	nd	nd	44,579.1
Pb	25.0	19.0	29.0
Zn	85.0	nd	nd

Fourier-Transform infrared spectroscopy (FTIR) gives an insight into structural changes in HA preparations as results of microbial activities. Figure 7 shows the FTIR spectrum of the original HA extracted from Mg-Rich soil and its alterations after incubation for 12 months in a microbial culture. In HA re-isolated from the culture sufficiently supplied with N (Figure 7b, c) a strong increase of a broad absorption band at 3,400 cm^{-1} was observed, whereas in a preparation re-isolated from a culture deficient in N (Figure 7d), rather a decrease at the same wave number could be observed.

This IR-feature indicates a strong participation of N─H structural groups in the respective HA preparation. Due to microbial growth in cultures deficient in N, these structural units were apparently eliminated. In the HA preparation isolated from the full-strength nutrient broth, the same structures remained unaffected, and in addition the presence of other N-containing units was documented by the amide bands I, II, and III at 1,652, 1,558, and 1,240 cm^{-1}, respectively. On the other hand, IR-absorption at 1,034 cm^{-1} (Si─O in mineral moieties), and that one at 468 cm^{-1} Si─O─Me^{+} bonds (Mg, Al, Fe) were diminished or almost depleted from the FTIR spectra of the re-isolated humic acids. This feature indicates an effective splitting of HA-metal-silicate complexes as result of microbial activities. This assumption seems further evidenced by an appearance of a C═O stretch at 1,736 cm^{-1} in the microbial re-worked HA from the Mg-Rich soil, i.e., at a position originally blocked up by metal ions bound in the HA preparations. I addition, the release of inorganic constituents from the HA preparations incubated in microbial cultures was also clearly documented by a strong decrease of ash contents in the HA which amounted up to 50% (Filip and Bielek, 2002).

TABLE 2. Colony forming units (CFU) of bacteria in soils with various contents of metals, and microbial species identified in cultures containing nutrient broth (NB) and enriched with humic acids (HA) from the same soils. (From Filip and Bielek, 2002.)



Soil sample	CFU g^{-1} soil	CFU ml^{-1} culture liquid		Microbial species identified in cultures
		After 7 days	After 21 days	
Control	7.3×10^5			
NB + HA		3.0×10^5	4.0×10^8	*Agrobacterium rhizogenes* *Alcaligenes latus* *Cryptococcus magnus* *Pseudomonas fluorescens* *Variovorax paradoxus* *Xanthomonas oryzae*
Metal-Rich	1.5×10^6			
NB + HA		3.0×10^7	1.4×10^9	*Cryptococcus albidus* *Cryptococcus terreus* *Pimelobacter simplex* *Variovorax paradoxus*
Mg-Rich	2.0×10^6			
NB + HA		3.0×10^6	4.0×10^8	*Cryptococcus albidus* *Cryptococcus magnus* *Pseudomonas fluorescens* *Pseudomonas marginalis* *Variovorax paradoxus* *Xanthomonas oryzae*

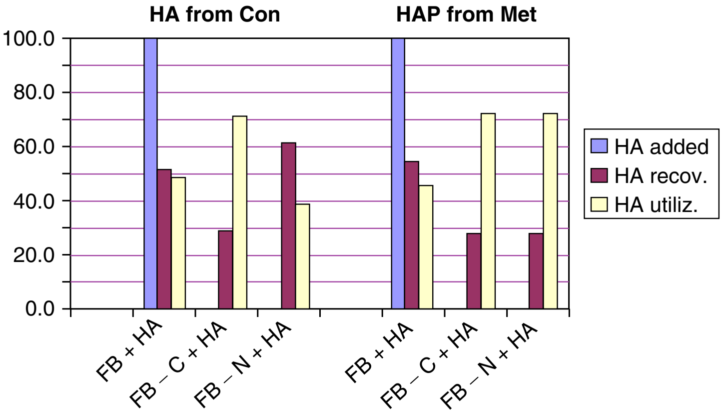


Figure 6. Microbial utilization of humic acids extracted from control (Con) and metal-rich (Met) soils. (From Filip and Bielek, 2002.)

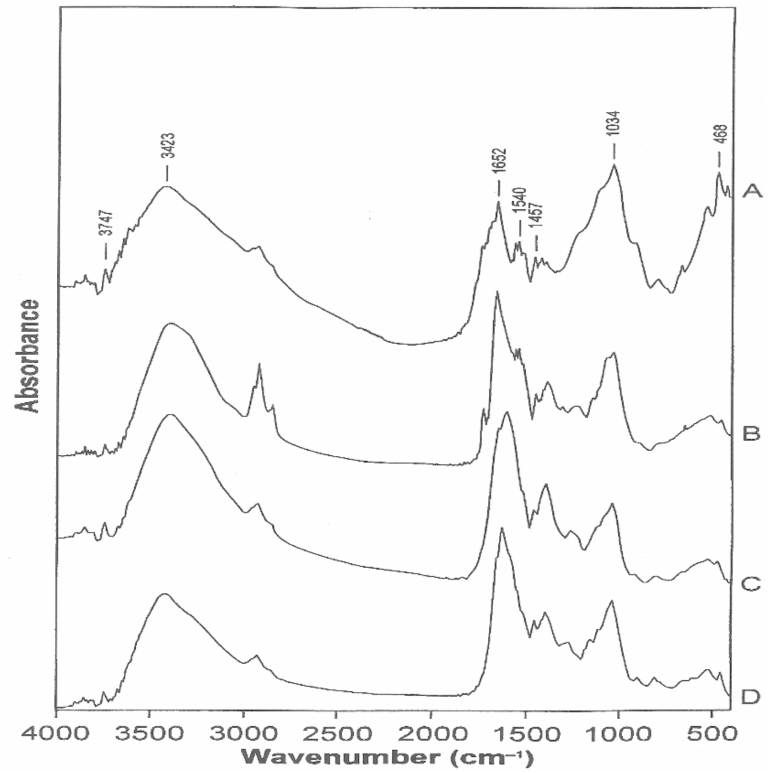


Figure 7. Fourier-transform infra-red spectra of (**a**) a humic acid preparation from Mg-Rich soil; (**b**) similar preparation incubated in a full-strength nutrient broth; (**c**) similar preparation incubated as a sole source of carbon; (**d**) similar preparation incubated as a sole source of nitrogen.

Recently, Cooke et al. (2007) reconstructed the presence of atmospherically derived metals such as Pb, Zn, Cu, Ag, Sb, and Ti in a deep lake sediment (usually containing an appreciable proportion of humic matter) as result of human metal smelting activities that occurred in a Peruvian mining region some 1,000 years ago. This curious finding indicates that upon anaerobic conditions a metal-organic-mineral matrix could be considered as resistant against degradation. Here, however, we demonstrated that under (semi-) aerobic conditions such as in liquid cultures, and especially if no easy utilizable nutrients are available, humic-metal-mineral complexes may undergo microbial decomposition resulting in release of the respective metal and mineral constituents.

5. Conclusions

Humic substances, and especially their complexes with metals and minerals have been often considered as widely resistant against biologic degradation. The results of our model experiments clearly demonstrate, however, that in the absence of easily utilizable nutrients humic-metal-mineral complexes can be efectively split down by a soil microbial population. Simultaneously the humic part of the complexes undergoes structural transformations.

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ENVIRONMENTAL MICROBIOLOGY, SOIL SCIENCE, NANOSCIENCE: A PLANETARY VIEW

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> *Scientific exploration of tiny soil particles, the planet Earth, or even the Universe: Basically, there is no difference in the matter. All this is truly multifarious, exiting, and finally useful to humans.*
>
> J. Konta, Charles University Prague (1957)
> (Modified by the Author)

Abstract. Nanoscience opened novel perspectives in many fields of science and technology in the twenty-first century. In soil and other environments, natural nano-sized systems such as clay minerals and humic substances exist and their interactions with biota strongly affect soil properties. Soil nanoparticles in some opposite to the engineered ones undoubtedly are capable of influencing metabolic activities of microorganisms. Different inter-planetary born inorganic and organic particles also appear nano-sized, and often they demonstrate structural analogy with soil components. Evidences also exist on the distribution of nanoparticles in the interstellar space, and their ejection to the planet Earth. These phenomena seem to open a rather unexpected view on the origin of the elemental soil constituents on the planet Earth.

Keywords: environmental microbiology, soil science, nanoscience, astroscience

1. Introduction

The term "nano" comes from a Greek word the meaning of which is "dwarf". As a technical term in a metric scale nano means a one billionth part, i.e., 10^{-9} of a unit. Thus, nanometer represents one billionth of a meter. The scientific community usually attributes the first acknowledgement of the importance of

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L.I. Simeonov and M.A. Hassanien (eds.), *Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology*,

the nanoscale range to the Nobel Price Laureate Richard Feynman who predicted already in 1959 that the properties of materials and devices in a nanometer range will result in a plenty of future opportunities (Imperiali, 2006). However, a particular progress in the field started in the 1980s. The invention of novel microscopic techniques such as Atomic Force Microscope, definitely opened a "nano-world" for researchers, and later on also for technologists. Now, in the last years, "nanotechnology" became almost a catch-all phrase in many respects. Even more, it is considered as the key technology of the twenty-first century (EC, 2004). Among other fields, nanotechnology could revolutionize agriculture, e.g., by linking nanosensors into a GPS system for the monitoring of soil conditions and plant growth, by enhancing the ability of plants to absorb nutrients, by detecting plant diseases rapidly, and also by using molecular methods to treat plant diseases effectively (Joseph and Morison, 2006). However, Dunphy-Guzman et al. (2006) pointed on the fact, that there is also a need for the weighting up both the benefits and possible risks of different applications of nanotechnology. Thus, in this respect it is to acknowledge that on behalf of the Executive Office of the President of the USA, the US National Science and Technology Council issued a comprehensive report in 2006 aiming to better identify research needs in environmental, health as well as safety related issues for all prospective nano-materials.

Due to a continuing self-assembly of individual atoms, molecules, or molecular clusters a plenty of natural organic and mineral nano-sized particles occurs in terrestrial and aquatic environments, and in planetary space, too. More than thirty years ago, e.g., Filip (1975) recommended the elucidation of inter-relationships between the smallest in size mineral and organic soil particles on the one hand, and microbial cells on the other hand, in order to better understand biogeochemical processes in soils and other natural environments. Since than, numerous studies on natural nano-scaled systems were carried out, most of them without having expressed the term "nano" implicitly. In the present contribution, a few examples of those approaches and their linkages to actual developments in different field of nanosciences should be presented.

2. Appearance and Importance of Natural Nanoparticles in Soil

Different inorganic, organic and biologic particles in soil appear in a size-range between less than 1 nm and up to 1 mm or even more. The size of amorphous silica, metal oxides, clay minerals, and their admixtures usually is less than 100 nm. In the same range, "nanobacteria" might appear, the existence of which, however, still remains controversial (Madigan et al., 2003). Nevertheless, bacteriophages and other viruses undoubtedly exhibit a nano-size. Clay minerals have been under special focus due to their multilayer structure, large specific surface area, and physical as well as chemical reactivity. Kaolinite, the main clay mineral in degraded soils, appears evidently nano-sized. In a chernozem and other soil types, similar is true for smectites, such as montmorillonite, the particle of which are a regularly less than 80 nm in size. Montmorillonite exhibits a large surface area (400–800 m^2 g^{-1}), and a cation exchange capacity up to 120 meq/100 g (Dixon and Weed, 1977). These and several others clay minerals readily form complexes with different organic compounds. In our model experiments, clay particles saturated with mono-, di-, or trivalent cations have been found capable of forming different in strength complexes with humic acids (Filip, 1968a). Humic acids themselves also appear as tiny nano-sized colloidal particles in soil (Beutelspacher and Van der Marel, 1968). In our experiments an enhanced formation of humic acid-like polymers was evidenced if montmorillonite was added to a nutrient solution in which the soil fungus *Epicoccum nigrum* grew (Filip et al., 1972). Also in our experiments, nano-sized clay particles exerted catalytic effects on polymerization of different phenolic compounds as evidenced by distinctly increased extinction values of the experimental samples (Table 1).

Evidently, clay minerals, different organic molecules and humic substances which represent the most important nano-sized particles in soils are involved in mutual reactions which result in the formation of organic-mineral complexes that strongly affect properties of the soil environment.

3. Effects of Natural and Engineered Nanoparticles on Microbial Activities

The interest in nanoscience increased especially after fullerenes were discovered in 1985. Fullerenes are macromolecules composed of pentagonal or hexagonal carbon rings which form a hollow sphere, ellipsoid, or tube. Usually, they are rather less reactive, but their reactivity can be increased by attaching different active groups to their large surfaces. Although fullerenes can be utilized in different technologies, sometimes they may become risky agents, too. Dhawan et al. (2006) reported genotoxic activity for low concentration of colloidal C_{60} fullerenes suspended in water. Limbach et al. (2007) found out that nanoparticles carrying some heavy metals could enter somatic cells by a Trojan-horse mechanism which provokes an up to eight times higher oxidative stress to cells than heavy metals added in a solution. Hyung et al. (2007) found nanotubes to settle to the bottom within an hour in flasks filled with clean water, but they remained dispersed for over a month if water contained indigenous organic (humic) substances. In a consequence, the aquatic humic matter might allow nanotubes to be transported in aquatic environments, and to interact with dissolved or suspended compounds, and surely also with organisms.

TABLE 1. Influence of muscovite on the browning reaction of pyrogallol in a sodium acetate solution at pH 6. (From Filip et al., 1977.)

Reaction mixture	Extinction values at 300 nm		
	After 4 h	After 24 h	After 48 h
Pyrogallol (PYR)	0.063	0.500	0.592
PYR + Muscovite-H^{1+}	0.076	0.750	1.260
PYR + Muscovite-K^{1+}	0.086	0.755	1.130
PYR + Muscovite Ca^{2+}	0.070	0.740	1.250
PYR + Muscovite-Al^{3+}	0.070	0.480	1.220

Recently, Tong et al. (2007) reported on the effects of fullerenes on the activity of soil microorganisms. A granular fullerene C_{60} was applied in aqueous suspension to samples of a silty-clay loam. Tetrahydrofuran residues (THF) generated during C_{60} formation process were also applied. As shown in Figure 1, the individual additions did not affect the CO_2 release from soil samples during a 30 day incubation period and the enzymatic activity in soil samples (ß-glucosidate, acid-phosphatase, urease) remained unaffected as well (not shown). The explanation is that the composition of microbial population remained unaffected from the additives as could be evidenced by the analysis of DNA extracted from soil samples.

Several decades ago, and somewhat opposite to the above mentioned results, we have established that a nano-sized clay particles (bentonite < 2 μm in size, and up to 0.5% w/w in amount) stimulated the growth of aerobic micro-organisms in soil samples (Filip, 1968b). The mineralization activity of soil microorganisms (CO_2-release) was enhanced in liquid cultures but not in soil samples (Filip, 1968c). The ammonification activity (NH_4-release) was only enhanced if an easily utilizable N-substrate was added soil samples (Filip, 1969). No correlation between the soil amendment with bentonite, and the total amount of humic substances was observed, but for fractions strongly adsorbed in soil samples a positive correlation was found (Filip, 1970). Different effects of clay minerals on the biochemical activity of soil microorganisms were evaluated in an early review (Filip, 1973). Later on, Filip and Hattori (1984) presented further evidences on how clays and other nano-sized particles influence the microbial utilization of substrates and transformation of solid substrata. Actual trends in the study of bio-, micro- and nano-systems were currently discussed by Filip and Demnerova (2007).

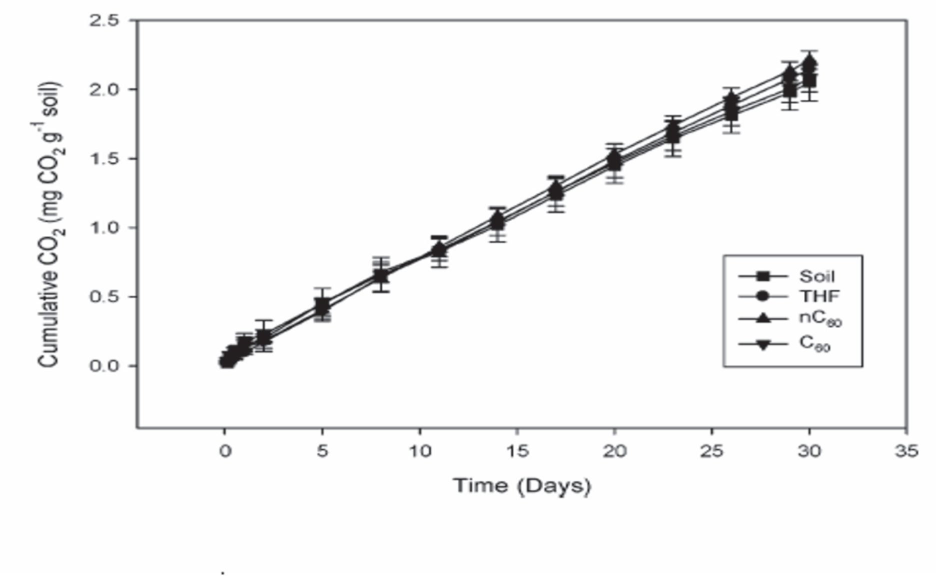

Figure 1. CO_2 release from control soil (■) or soil treated with granular fullerene C_{60} (▼), aqueous dispersion of C_{60} (▲), or with THF-C (●). (Tong et al., 2007.)

4. Natural Ties between Planetary Born Particles and Soil

About 12 billion years ago, a Big-Bang occurred, and all space became flooded with photons, x-rays and γ-rays, and since then the Universe still remains flooded by radiation (Oro, 2000). Apparently, the greatest change in the history of the Universe was the transformation of radiation into matter. Such a process could be justified by means of mathematics (Chaisson, 1998). The cosmic evolution from its very beginning and until today apparently occurred in a following sequence (Chaisson, 2000):

Energy→Particles→Atoms→Galaxies→Stars→Planets→Life→Intelligence→Culture.

As a general trend an overall increase in complexity from chaos to order, and from inorganic to organic with the march of time can be recognized. Soon after a Big-Bang occurred, hydrogen was formed in the process of primordial nucleosynthesis. Consecutively, helium was formed by hydrogen burning, than by burning of helium the element carbon was created, and the direct nuclear burning continued further with the formation of oxygen, neon, magnesium, silica, and so on. The synthesis cumulated in the formation of iron, the heaviest element apparently formed through direct nuclear burning (Kwok, 2004). The atomic form did not remain the only one in which elements occur in the Universe. Molecules are other major constituents of planetary atmospheres.

About 120 different molecules have been detected using spectroscopic methods, and they were listed individually by Oro (2000). In a circumstellar dust of asymptotic giant branch (ABG) stars, Posch et al. (2002) detected the presence of a variety of refractory Al-, Mg/Al-, and Mg/Fe-oxides. Also in soil, mutual interactions exist between amorphous Al-, Fe-, and Mg-oxides and soil organic substances (Huang and Violante, 1986; Schwertmann et al., 1986). In general, and likely in the Earth’s crust, silicon apeares as the most abundant elements in the Universe. However, the abundance of crystalline silicates seems rather small in comparison to amorphous forms. According to Kwok (2004), several authors also proposed the presence of nano-sized hydrogenated amorphous carbon grains, nano-diamonds, TiC-nanoclusters, and hydrogenated fullerenes in stellar environments.

As reported by Oro (2000) the interstellar dust and carbonaceous chondrites undoubtedly consist of different aliphatic and aromatic organic compounds (Table 2). Similar compounds have been repeatedly identified in different soils, sediments and humic substances (Filip, 1978; Filip and Alberts, 1994; Filip et al., 1999; McKeague et al., 1986). From results obtained by Pendelton and Allamandola (2002), Kwok (2004) developed a comprehensive model of carbonaceous interstellar dust (Figure 2) was developed by Kwok (2004). Evidently, a strong compositional resemblance exists to structural models of soil humic acids (Figure 3) as published earlier by Schulten (1994).

TABLE 2. Organic compounds identified in stellar environments. (From Oro, 2000.)

Compound type	Concentration (ppm)	Number of identified compounds
Aliphatic hydrocarbons	>35	210
Aromatic hydrocarbons	15–28	87
Alcohols and polyhydroxy comp.	11	8
Aldehydes and ketones	27	9
Carboxylic acids	>300	42
Dicarboxylic acids	>30	67
Hydrocarboxylic acids	15	51
Amines	8	10
Amides	55–70	4
Amino acids	60	78
Purines and pyrimidines	1–2	5
Other heterocycles	7	32
Sulfonic and phosphonic acids	5	12

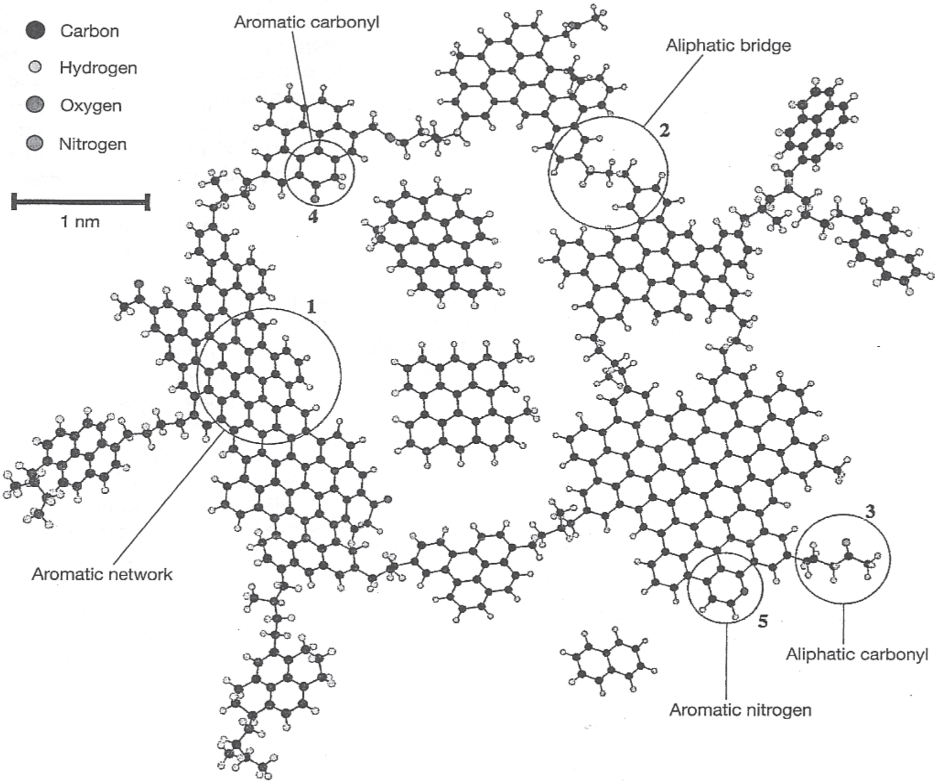

Figure 2. Structural model of carbonaceous interstellar dust consisting of various aromatic and aliphatic components. (From Kwok, 2004.)

Both inorganic and organic solid-state compounds are regularly ejected into interstellar medium, and the macromolecular carbon-bearing materials represent major components of planetary surfaces throughout the solar system (Cruikshank, 2000). Flynn et al. (2000) made a calculation based on a presumption that interplanetary organic particles sized from 50 to 25 nm would not be heated above 900 K in part, and therefore not pyrolyzed when striking the top of the Earth's atmosphere. Taking the organic content of these particles as 2–10 weight-percent, he estimated that interplanetary dust contributes from 6 to 30 t y^{-1} of organic matter to the Earth in the present era. During the first 0.5 billion years of the Solar System history, the contribution of organic matter to the Earth by the accretion of interplanetary dust may have been much greater. Oro (2000) concluded from his and other author investigations that comets that arrived in the early phase of solar system formation from the Jupiter region also served sources of organic and other material (10^{21}–10^{26} g), and in addition they might have become a major source of terrestrial water. Consecutively, the presence of liquid water and different simple organic and inorganic interstellar compounds eventually resulted in the emergency of the first simple forms of life on our planet. In this connection it is to admit, that studies of sedimentary rocks from South Africa and Western Australia indicated the evidence of CO_2 fixing microorganisms on Earth as early as 3.5 Gy ago.

5. So, What Is Soil?

A question might appear, whether or not facts documented and discussed here would formally fit into a current system of soil science, and whether they could contribute to a better understanding of the origin of soil? Some of the classicists in the field of soil science such as Kostychew (leading Russian soil scientists of the nineteenth century) would probably agree with such an assumption. In a monograph, he accounted the elucidation of the origin of soil structural components as a fundamental part of soil science. On the other hand, Viliams (also a Russian soil scientist) wrote just in his introduction to a 1940s issue of the Kostychew's text-book quite decisively that any understanding of soil basically depends on the understanding of plant physiology because soil science could not be divided from plant sciences (Kostychew, 1940). Nevertheless, some decades later, Mückenhausen (1975) included a chapter entitled "Die Erde als Himmelskörper" as a natural introduction into his text-book of soil science. Actually, in a review on a topographic signature of life, Dietrich and Perron (2006) claimed a recent soil formation as driven solely by non-biotic processes, i.e., in the absence of any vegetation. In the Atacama Desert in Chile, a hyperarid region, extensive areas of rounded soil mantles topography exist in which biological processes are essentially absent. This soil resembles strongly to Columbia Hills at the planet Mars as documented by scientific photographs and other data obtained from a Mars Exploration Rover.

In fact, the surface of Mars contains an abundance of landforms which resemble to those on Earth, and in this respect Mars seems not to be an exception among the planets in the Solar System. Tsapin et al. (2000) reported that a moisturizing Martian soil results in the evolution of oxygen. Furthermore, if a bacterial nutrient solution was added, $^{14}CO_2$ along with some oxygen was released from the Martian soil. Since iron is one of the most abundant elements in Martial surface material, ferrate-ions (Fe^{6+}) which are known as strong oxidants are apparently responsible for the reactions in behind of the observed phenomena.

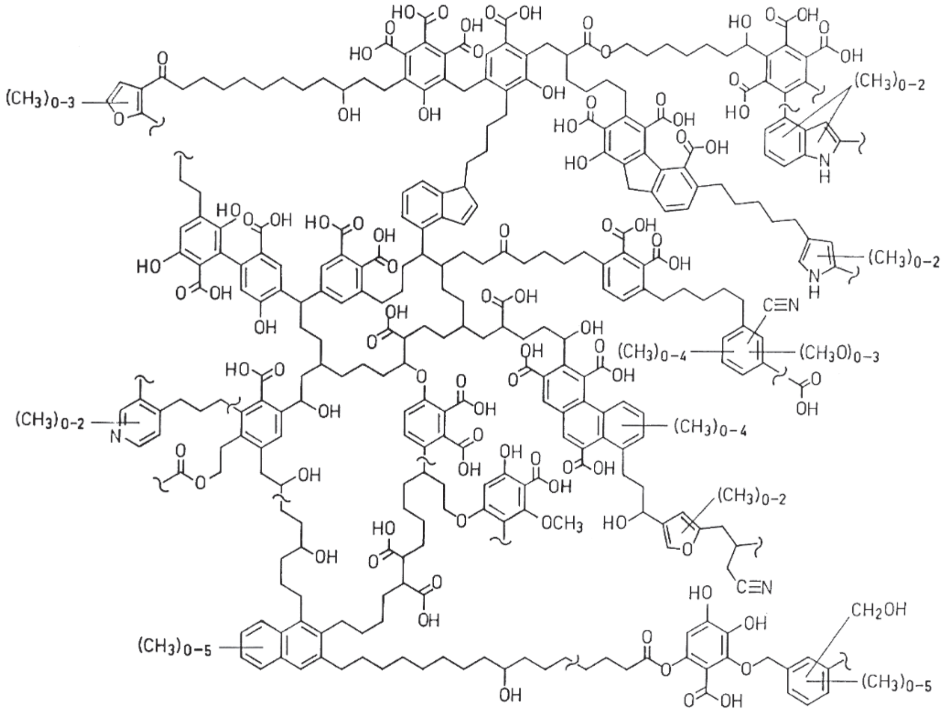

Figure 3. Complex structural concept for soil humic acids. (From Schulten, 1994.)

On the surface of Titan, another planet in our solar system, valley networks exist similar to those which dominate the surface of the Earth. Titan atmosphere contains a large amount of N_2 and, perhaps water pools on the surface that might originate from meteorites strikes (Simakov, 2000). Due to these conditions, Titan appears to be a candidate for the next emersion of life in the far future, perhaps, after the life on our planet Earth will be extinguished.

6. Conclusions

There is no doubt that soil represents a natural body consisting of different nano-sized mineral and organic particles. It is to expect that some of these soil components will comprise novel technological applications. Novelties can be expected primarily in the field of soil biology. If the existence of nano-sized organisms will be confirmed and their participation in biogeochemical processes experimentally documented, than novel applications in a broad field of (soil) biotechnology could be developed. Based on the existing knowledge, however, both the origin, characteristics, and importance of nano-sized mineral and organic soil constituents undoubtedly deserve to be scientifically reconsidered because they roots apparently penetrate deep in the history of the Universe.

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ENVIRONMENTAL EFFECT ASSESSMENT OF ORGANIC PBT COMPOUNDS

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Abstract. PBT is the abbreviation of persistent, bioaccumulating and toxic compounds (materials); vPvB chemicals are very persistent, very bioaccumulating compounds. Both type of materials exist for a longer period in the environment. These all are persistent organic pollutants (POP) that disperse in the environment and exert effect on distant territories too. PBT or vPvB? Difference is not so sharp in the reality. Dangers source from bioaccumulation and/or biomagnification (multiplicative effect) after or during bioaccumulation period. Scientifiic and civil communities have to think on acceptability of these chemicals else more than half of existing compounds should be excluded from daily usage. There are additional dangers of chronic exposure that can cause unrequested side effects, destroy integrity of endocrine system and can be hardly measured by conventional tests. We composed a preliminary PBT assessment methodology as a possible first approach to determine the PBT properties of an organic compound with the aspect of determining direction of further investigations. Importance and application of PBT assessment: we can predict the real danger of compounds not tested yet without additional costs and in short time considered to be as an advantage of the approach, especially in case of non-existing data. This method is more exact than traditional ones because applying just risk factors can be overt based on precautionary principles. An overt application of risk factors can restrict the broad application of a compound. Assessing existence of PBT danger as a part of hazard evaluation of compounds are based on PBT aspects that can be done with help of (Q)SAR-models (Quantitative/Qualitative Structure Activity Relationship) and/or applying PBT-vPvB criteria and/or EPIWIN and additional programs in case of non-existing experimental and monitoring data. We consider some aspects of REACH (new European chemical regulation) requirements too.

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Keywords: PBT, hazard assessment, risk assessment, chemical safety assessment, authority viewpoints

1. Introduction

PBTs are persistent, bioaccumulating, toxic compounds; vPvB chemicals are very persistent, very bioaccumulating compounds, delay for a longer period in the environment. These are persistent organic pollutants (POP). PBT or vPvB: If a chemical refers to a P or vP criteria, then it has long environmental half-life and exert a potential danger to the environment. It conclude in a detrimental or deleterious effect sourcing from a chronic exposition that can not predicted by standardized laboratory tests. Dangers of chronic exposition: organism tries to get rid of xenobiotics but during this time occur an accumulation of material and/or any effect. It can decrease the ability (power) of immune system and/or cause erroneous signalization and additional unrequested side effects. Our chosen example case PCB-77. It can danger the integrity of endocrine system. Dangers to the environment: disperse in the environment, exert effect on distant territories too. Where will they accumulate and on what kind of living organisms they exert a deleterious effect? If toxic material is not just persistent in the environment, but bioaccumulating too, then expositional potential exerted on living organisms of higher trophic level is higher. Dangers source from bioaccumulation and/or biomagnification (multiplicative effect) after or during bioaccumulation periode. Application and importance of PBT assessment: we can predict the real danger of compounds not tested yet without additional costs assessment in case of non-existing data (OECD, 2005). Characteristics of PBT assessment: Presently, this kind of assessment does not cover all possibly affected organisms, just some key organisms but after clarification of toxicity rules will be available and extendable to additional organisms. This method is more exact than traditional approach, applying just risk factors that can be overt based on precautionary principles. An overt application of risk factors can lower the broad application of a compound. Applying it less than necessary will increase the risk. Assessing existence of PBT danger: Possibility of assessing dangerousity of compounds are based on PBT international criteria (Q)SAR-models (Quantitative/Qualitative Structure Activity Relationship), already existing data of the same (similar) compounds and/or applying PBT-vPvB criteria (Tables 1 and 2) and/or EPIWIN and additional programs (Epiwin, 1986). Practical approach: applying all of the above mentioned ones at the same time.

TABLE 1. Criteria for identification of PBT and vPvB substances. (From EU, TGD 2003.)

Criterion	PBT-criteria	vPvB-criteria
P	Half-life > 60 days in marine water or >40 days in freshwater or half-life > 180 days in marine sediment or >120 days in freshwater sediment	Half-life > 60 days in marine- or freshwater or >180 days in marine or freshwater sediment
B	BCF > 2,000	BCF > 5,000
T	Chronic NOEC < 0.01 mg/L or CMR (having carcinogenicity, mutagenicity or reprotion toxicity) or endocrine disrupting effects	Not applicable

TABLE 2. International criteria for categorization of PBT results. (From ENV/JM/TG (2005)5/REV1.)

	Persistence	Bioaccumulation	Toxicity
EU PBT (based on TGD)	Half-live >60 days in marine water or >40 days in fresh water >180 days in marine sediment or >120 days in fresh water sediment	BCF > 2,000	Chronic NOEC < 0.01 mg/L or avial chronic NOEC < 30 mg/kg/food or CMR 1 or 2 or evidence to other chronic toxicity (e.g. endocrine disruption, heavy damage due to long exposition)
EU vPvB (based on TGD)	Half life >60 days in marine water fresh water or >180 days in marine, fresh water sediment	BCF > 5,000	Not applicable
OSPAR PBT criteria	Not biodegrading or half life >50 days in water	Log $K_{ow} \geq 4$ or BCF ≥ 500	Acute toxicity on water organisms L(E)C50 ≤ 1 mg/L or long term NOEC ≤ 0.1 mg/L or mammal toxicity: CMR or chronic toxicity
UNEP	Half life >2 or 6 months in water; >6 months in soil/sediment; or any other evidence,	BAF/BCF > 5,000 or log $K_{ow} > 4$ or 5; monitoring results or any other evidence	Based on chronic toxicity or ecotoxicity data dangerous on human health or environment because of long term

POP	according to the material persistent enough	that material in spite of lower BAF/BCF value bioaccumulating	transport
US-EPA – National PBT Strategy	Half life: >56 days (high); 7–56 days (intermediate); <7 days (low)	BAF > 5,000 (high); 1,000–5,000 (intermediate); <1,000 (low)	Materials on one or more toxic material list(s)
Canada – Toxic substance handling	Half life: in air >2 days, in water >2 months, in sediment >1 year, in soil >6 months	BAF or BCF > 5,000 or log $K_{ow} > 5$	Inherently toxic

2. Description of Method

Global models were created from quite different chemicals with available endpoint results but local models build on more restricted pool of compounds (e.g. congeners, similar compounds). As a practical first approach we apply validated global or generic (e.g. EPIWIN) and local or specific models (e.g. TOPKAT) and additional values of endpoints of similar compounds from different databases parallelly to be able to cover all the unknown properties of a compound. To get confidence about results to be able to support and/or propose additional really necessary toxicological examination we gather data from different databases about the chemical and about very similar chemicals (based on structural and endpoints similarity). As a basic approach based on Annexes of REACH (new European chemical regulation) and as part of Chemical Risk Assessment we have to gather all available information about a chemical compound and its component and its main metabolites to be able to find possible controversions in materials that are subject to authorization. Although a preferred order is proposed as P first, B second, T third, with help of the above method a parallel elaboration is possible. This way we shall be able to know where this new method is not applicable and why. To get all the data to further decisions we have to apply the scheme drawn in Figure 1. With results of PBT assessment we can provide a basis and a certain confidence about necessity of additional tests. Of course to a final decision supporting additional test all the information requirements have to be comply.

2.1. EXAMPLE OF ASSESSMENT OF PERSISTENCE, BIOCONCENTRATION, TOXICITY OF PCB-77 WITH EPIWIN

As an example of some demonstration of application of a global model we chose PCB-77 (3,3’,4,4’-tetrachlorobiphenyl) that will be subject yet to additional tests in our institute.

Assessment starts with converting the molecule into SMILE (Simplified Molecular Input Line Entry): c2cc(CL)c(CL)cc2-c1ccc(CL)c(CL)c1. Such conversion will be necessary mainly in case of new or unregistered compounds.

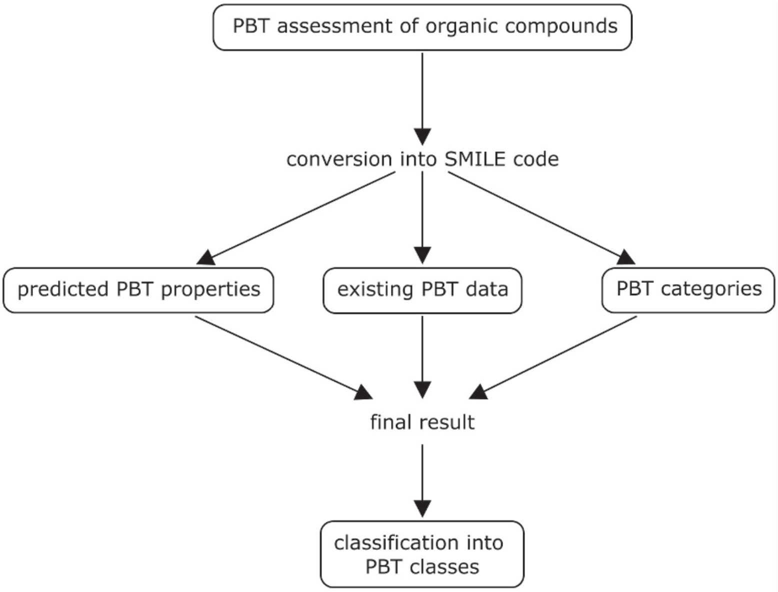

Figure 1. PBT assessment of organic compounds.

2.1.1. *Assessing Persistence*

As a first approach to PBT assessment according to the REACH process proposals we apply different QSARs parallelly from different sources (e.g. EPIWIN, TOPKAT) and databases (as EINECS, TOXNET, MITI (2008)), limit values from TGDs (Technical Guidance Document) to get direct values to existing endpoints and to compare them with predicted ones from validated models.

2.2. EXAMPLE PERSISTENCE ASSESSMENT OF PCB-77 WITH BIOWIN (US EPA)

Biowin1 (linear modell): not biodegrades fast

Biowin2 (non linear model): not biodegrades fast

Biowin3 (final biodegradational periode): calcificant

Biowin4 (primer biodegradational time frame): weeks

Biowin5 (MITI linear model): not easily degrades

Biowin6 (MITI non linear model): not readily biodegradable

Assessment of Easy biodegradability: NO

Biowin1 modell FRAGMENTS	Coefficient	Value
Frag | 4 | aromatic chloride [–CL]	–0.1824	–0.7297
MolWt| * | molecule weight parameter		–0.1390
Const | * | equation constant		0.7475
Result -> probability		
Biowin1 (Linear Biodegradation Model)		–0.1211

>0.5 --> degrades fast

<0.5 --> not degrades fast

BIOWIN offers more possibility to determine biodegradability of a molecule (compound) (Boethling et al., 2004). The result is a probability value. If the value is over 0.5, then the molecule is more possible to degrade fast, if its lower then 0.5 the molecule is more possible to be persistent. Final decision about biodegradability comes from six different built-in models that have different predicting power. Additionally to that we get a biodegradational time frame result too with an approximate degradation time periode. This periode is a result of a predicted classification according to the following values.

Classification of result: 5.00 -> hours 4.00 -> days 3.00 -> weeks (primer and final) 2.00 -> months 1.00 -> more longer.

In the models molecule fragments and molecule weight modify the probability of biodegradation and the result is a linear combination of values due to the found (characteristic) fragments of molecule and the molecule weight (Howard et al., 1987). In our case PCB-77 is a persistent molecule according to the result – 0.1211 (lower than 0.5) of model Biowin1 and biodegradation of the molecule delays for weeks according to Biowin4.

2.3. DECISION ABOUT PERSISTENCE

Choosing from most realistic results (two with less then 10% difference from tree) or median of more results (at least three different with less then 10% difference).

2.4. ASSESSING BIOACCUMULATION

The most simple approach to determine bioaccumulation in case if there is no measured or monitoring data is to get a predicted BCF value with BCFWIN module of EPI Suite that predicts BCF values based on log K_{ow} models (US EPA OPPTS, 2002). This is not straightforward in every case because bioconcentration can be modified on different factors such as e.g. molecule size, biotransformation by different microorganisms. So log K_{ow} is not always the best predictor basis for models especially over value 6.

2.5. EXAMPLE OF BIOCONCENTRATION ASSESSMENT OF PCB-77 WITH BCFWIN (US EPA)

Formula: C12 H6 CL4

Molweight: 291.99

Bcfwin v2.15

log K_{ow} (predicted): 6.34

log K_{ow} (experimental): 6.63

BCF from log K_{ow}: 6.63

BCF equation at prediction

$$\log BCF = 0.77 \log K_{ow} - 0.70 + \text{correction}$$

Correction value:

Multihalogenized biphenyl/PAH 0.620

Predicted log BCF = 5.025/BCF = 1.059e + 005

The result of the model is based on log Kow and a correction value that is in our case a multihalogenized biphenyl/polyaromatic hydrocarbon: 0.62, and the predicted BCF value (1.059e + 005) is over 5,000 that is the compound is bioaccumulating (B).

2.6. ASSESSING TOXICITY

Applying global models we can predict a result that may be realistic or not so close to the real value. Therefore, it is necessary to apply a local model too in order to refine result and lower uncertainty. If results from different sources are far from each other, then additional possibly close results are needed from a similar compound. Results that we get this way in different toxicity endpoints are acceptable for REACH purposes if we support it with consequent evidences.

2.7. EXAMPLE OF TOXICITY-ASSESSMENT WITH EPIWIN

In this example below we have to pay attention to water solubility and to log K_{ow} cut-off values of different endpoints. If we can not draw a conclusion, then additional examination (test) is needed.

Water solubility: 0.04859 mg/L (computed)
Predicted class – neutral organic compound

Organism	*Duration*	*Endpoint*	*mg/L (ppm)*
Fish	14 days	LC50	0.065 *
Fish	96 h	LC50	0.018
Daphnia	48 h	LC50	0.026
Green algae	96 h	EC50	0.021
Fish	30 days	ChV	0.005
Daphnia	16 days	EC50	0.009
Green alga	96 h	ChV	0.026
Fish (SW)	96 h	LC50	0.034
Mysid shrimp	96 h	LC50	0.000235
Earth worm	14 days	LC50	82.728* mg/kg dry mass of earth

(* compound can not be solved in water!)

Fish and daphnid acute toxicity log K_{ow} cut-off: 5.0
Alga EC50 toxicity log K_{ow} cut-off: 6.4
Chronic toxicity log K_{ow} cut-off: 8.0
Molweight cut-off: 1,000
where LC50: lethal concentration
ChV: chronic value
EC50: effective concentration

2.8. FINAL DECISION

How to come to a final decision about PBT characteristics of a compound? As a practical approach applying all of the above mentioned approaches and tools:

- Choose the most relevant and applicable criteria from international PBT criteria (Table 2) and insert those criteria into our regulatory scheme.
- Apply global and local validated (Q)SARs, possibly with known applicability domain (determined by the respective authors). This is an initial way to the combined use of QSARs and multicriteria decision making (Cronin et al., 2003).
- Use existing data from different databases to the same (or similar) compound.

If data from different sources supporting each other and there is no contradiction and the value is positive, then we can accept it, else we have to propose further examination first of all just on directions where results were controversial. At international PBT regulatory schemes BCF > 5,000 is applicable for purpose of our unified decision process that is mainly based on EU PBT criteria. NOEC < 0.01 mg/L chronic toxicity or existing data if either mammal toxicity or CMR applicable at the toxicity criteria. Assessments and criteria built into one flow chart that can be part of an initial step of an integrated REACH Risk Assessment Procedure (EC, 2003). Assessment of persistence, bioaccumulation and toxicity with different existing models can lower the uncertainty of above mentioned properties, especially in case of HPV materials without existing toxicological result.

2.9. EXAMPLE OF APPLYING PBT CRITERIA

If we have all the results, not just from parent compound but from its major metabolits regarding PBT properties, according to the most relevant and applicable international PBT criteria (Table 2) we can come to a partial or full PBT classification decision. In case of mixtures all the major components are needed and PBT criteria are subject to all major component separately.

In Figure 2 we decide between persistence and easy degradability. If material is easy degradable and not toxic but there is any major metabolite that is toxic, then we come to a "toxic" (T) decision.

In Figure 3 we decide about bioaccumulation. If BCF > 5,000 and/or as support log $K_{ow} > 4$, then we have to consider the chemical as bioaccumulating, if it has not toxic but bioaccumulating metabolites, then the material is a PB or a PBT, if it has toxic metabolite. Chemicals with "just PB" property can cause any disturbance in organisms even if it doesn't seem to be toxic.

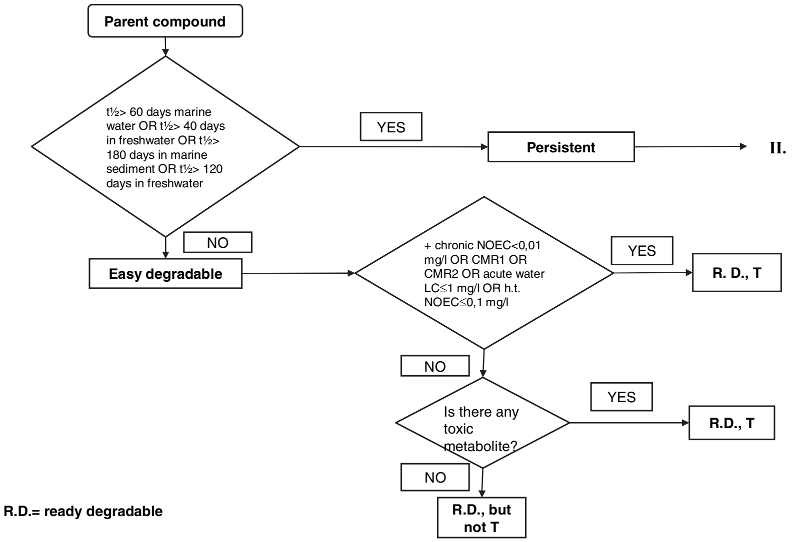

Figure 2. Criteria and PBT decision steps I.

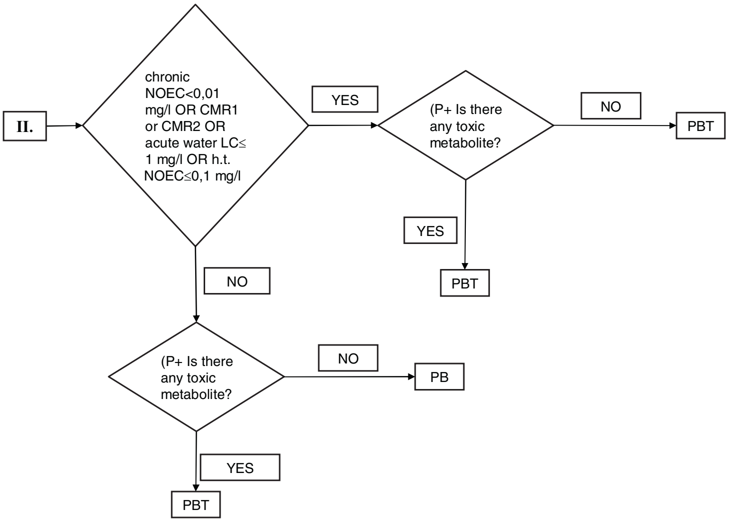

Figure 3. Criteria and PBT decision steps II.

In Figure 4 we have already three cases in which we can classify a compound as PBT and one case when it is “just PB” and this is in the case if neither parent compound nor its metabolite seem to be toxic.

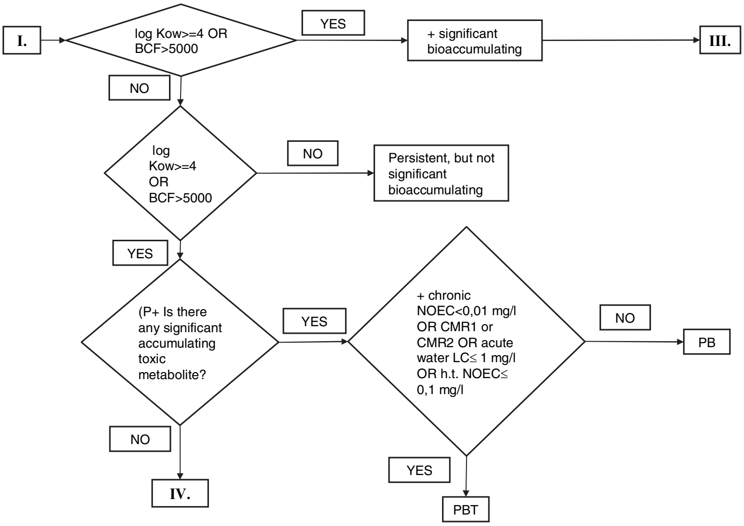

Figure 4. Criteria and PBT decision steps III.

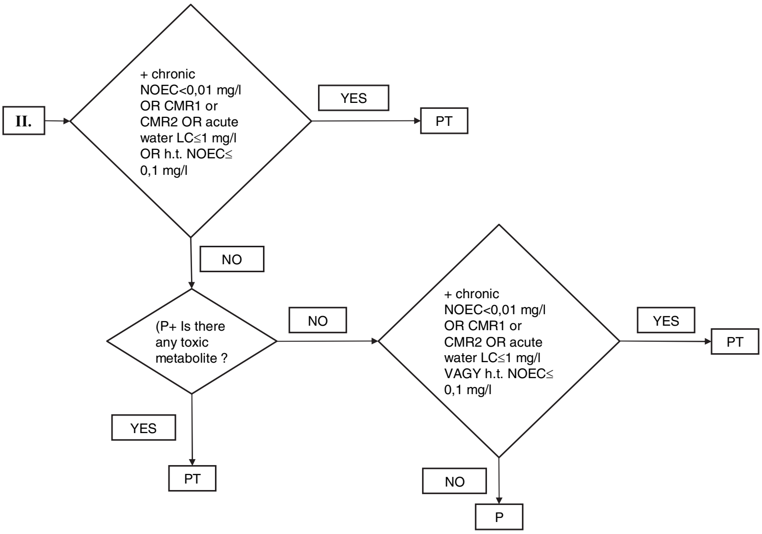

Figure 5. Criteria and PBT decision steps IV.

In Figure 5 we decide between a persistent (P) or “just PT” characteristic of that material. In case of “PT” materials we can have similar concerns as by PBT materials but the difference in their health effect is not an easy task to settle.

2.10. PBT/vPvB ASSESSMENT AND REACH

According to REACH: „The objective of the PBT and vPvB assessment to determine if the substance fulfils the criteria given in Annex XIII and if so, to characterise the potential emissions of the substance. A hazard assessment … addressing all the long-term effects and the estimation of the long-term exposure of humans and the environment as carried out … (Exposure Assessment), step 2 (Exposure Estimation), cannot be carried out with sufficient reliability for substances satisfying the PBT and vPvB criteria in Annex XIII. Therefore, a separate PBT and vPvB assessment is required. ((EC) No 1907/2006: 4.0.1).

The PBT and vPvB assessment shall comprise the following two steps, which shall be clearly identified in the Chemical Safety Report:

Step 1: Comparison with the Criteria
Step 2: Emission Characterization

The assessment shall also be summarised in the Safety Data Sheet ((EC) No. 1907/2006).

2.11. COMPARISON WITH THE CRITERIA

“This part of the PBT and vPvB assessment shall entail the comparison of the available information, which is submitted as part of the technical dossier, with the criteria given in Annex XIII and a statement of whether the substance fulfils or does not fulfil the criteria. If the available information is not sufficient to decide whether the substance fulfils the criteria in Annex XIII, then other evidence like monitoring data available for the registrant and giving rise to an equivalent level of concern shall be considered on a case-by-case basis. If the technical dossier contains for one or more endpoints only information as required in Annexes VII and VIII, the registrant shall consider information relevant for screening for P, B and T properties to decide whether further information needs to be generated to fulfil the objective of the PBT and vPvB assessment. In case the generation of further information is necessary and would require testing on vertebrate animals, the registrant shall submit a testing proposal.” ((EC) No 1907/2006) The next step would be Emission Characterisation where we could use the results got by PBT assessment. Assessment of persistence, bioaccumulation and toxicity with different existing models establish a good basis for Chemical Risk Assessment. This means that our approach can be applied in connection with starting REACH in case of produced materials with quantity above 1 t/a. This method steps over of a screening level assessment because it concentrates on not just applying risk factors but tries to get the most possible and relevant environmental risk values. Although even if factors cannot be excluded in every case but uncertainty can be lowered. This directed approach with its inner details draws attention to the most dangerous materials that in certain cases require additional examination(s) to verify their (industrial) application safety or their final exclusion.

3. Conclusions

What to do with the results of PBT assessment? Where a Chemical Safety Report is required, the results of the PBT assessment as set in the Chemical Safety Report shall be given. There is practically not a big difference between PBT and vPvB compounds. We assessed PBT characteristics of more than 100 compounds (data not shown) and results could be established just with BCF ≥ 5,000 (and not less) else more than half of existing compounds had to be excluded from its daily usage. Acute and chronic toxiciy limit values for the existing endpoint are applicable. Instead of BCF or beside of it we could use BAF (predicted BAF, especially in case if a compound easily adheres to sediment but BCF is not measurable because of its low solubility) but this approach have to be examined yet.

If PBT assessments reported in the Safety Data Sheet is appropriate, then no further hazard assessment or PBT and vPvB assessment is necessary. In this case the relevant information reported by the supplier for the risk characterisation can be used and stated in the Chemical Safety Report (created by Chemical Safety Assessment).

A Chemical Safety Assessment of a substance shall include the following steps:

(a) Human health hazard assessment
(b) Physicochemical hazard assessment
(c) Environmental hazard assessment
(d) Persistent, bioaccumulative and toxic (PBT) and very persistent and very bioaccumulative (vPvB) assessment

Assessment of persistence, bioaccumulation and toxicity with different existing models can lower or lowers the uncertainty of the respective PBT properties. Especially in case of HPV materials without existing toxicological result. In connection with starting REACH this approach can be very helpful already in cases of produced materials with quantity above 1 t/a since we have to prioritize or at least propose a prioritization among actual registered materials based on the view of most possible dangerousity of materials. We can conclude that this approach steps over a screening level assessment because we don't have to rely on just scarce or ambivalent information to decide.

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RISK ESTIMATES OF AIR POLLUTANTS IN DEVELOPING COUNTRIES

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Abstract. Air pollution has become an increasingly important environmental issue in the entire world and in particular developing countries. High levels of suspended particulates have become a common parameter of many regions. Emissions of gases have been rising steadily as industrialization occurs. Projections indicate that potentially large increases in emissions may occur during the next 20–50 years if current development patterns persist. Local concentrations of air pollutants depend upon the strength of their sources and the efficiency of their dispersion. It was also well understood that air pollution is responsible for many aspects of human health, inefficiency and loss of environmental productivity. It was also realized that natural air pollution may be synergistic with some specific anthropogenic air components leading to prospects of higher damage to health, materials, productivity and economy. Nowadays, air quality is taken as a major aspect of the quality of life leading to sustainable development in many areas of the world. Risk assessment of air pollutants is based on a single question; is the ambient concentration above a level considered to pose a risk to the population?

Keywords: air pollutants, developing countries, risk assessment, case studies

1. Introduction

1.1. AIR QUALITY IN THE DEVELOPING COUNTRIES

Air pollution has become an increasingly important environmental issue in the developing countries. Air pollutants have damaging effects on materials and

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vegetation through influencing deterioration rates of materials and agricultural productivity of land. They impose aesthetic damages ranging from reduced atmospheric visibility to reduced property values. Local sources including urban growth, transportation systems, industrialization, and lack of awareness and shortage of institutional capabilities all contributed to the relatively low air quality and weak control. Among the most common air pollutants normally used as air quality indicators, are sulphur dioxide (SO_2), nitrogen oxides (NO_x), suspended particulate matter (SPM or PM_{10}), carbon monoxide (CO) and ozone (O_3). Major types of pollution sources in these countries such as dust storms and sandstorms, greenhouse gas emissions and other gases from various industries are outlined in Table 1.

TABLE 1. Sources and impacts of air pollutants.

Pollutant	Cause	Effects
Particulates, PM_{10} (fumes, dust, etc.)	Fuel combustion	– Damage to respiratory system – Damage to vegetation – Corrosion
Carbon monoxide (CO)	Incomplete fuel combustion	– Blocks oxygen transport to body tissues. ($HBO_2 \rightarrow COHb$)
Carbon dioxide (CO_2)	Complete fuel combustion	– Green house effect, and global warming
Nitrogen oxides (NO_x)	Combination of N_2 and O_2 during combustion processes.	– Eye and lung irritation – Forms acid rain
Ozone (O_3)	Reaction of NO_x with HC in the presence of sunlight	– Respiratory irritation – Eye and nose irritation
HC and VOC	Liquid and unburned fuels	– Eye and respiratory irritation – Photochemical smog
Lead (Pb)	Lead-containing fuel	– Severe toxic effect on human bodies – Lower IQ in children

The developing countries, however, will face intensified environmental problems as a result of population growth, economic development, and rapid urbanization. An increasing number of cities will face the serious air and water quality problems. Unlike some of the other major problems, there is a high chance that the air pollution problems can be solved if preventative measures are put in place early before air pollution gets out of hand. Improvements in environmental quality would mean reducing the magnitude of these adverse effects. Investigation of the quantitative significance of these effects is integral to the formulation and implementation of environmental policies aimed at improving quality of life. The aim of protecting the air environment from pollution is to achieve the following objectives:

1. To protect the air that people breath from any hazards in all their forms
2. To assess the environmental impact on the health of people
3. To find a way to decrease the pollution from the point sources

Many countries in Africa have not yet reached the level of economic development and industrialization experienced in other parts of the world. Opportunities exist to avoid the human and environmental costs of economic development resulting from air pollution by learning from other countries and taking appropriate preventive action. By initiating AQM measures at the early stages of economic development, countries can avoid the severity of air pollution impacts and achieve better air quality.

1.2. AIR POLLUTION SCENARIOS IN DEVELOPING COUNTRIES

It is estimated that the mean amount of dust fallout along the coastal area of Kuwait may reach up to 1,002.7 t/km^2 with an overall mean of TSP equal to 207.8 μg/m^3. Total solid particulates (TSP) in Damascus air is estimated at 749 μg/m^3 in highly congested traffic areas and 333 μg/m^3 in residential zones. Hassanien et al. (2001) reported that annual concentration of TSP ranged from 59–987 μg/m^3 with average of 397 μg/m^3 over Cairo during the period 1992–1997. Recently, Hassanien (2006) found that PM concentration in a residential urban area was ranged from 134–750 with average of 384 μg/m^3. Particulate matter level in Greater Cairo area are characterised by long rang spatial and long term temporal distributions, which are probably created by meteorological conditions. Other development activities and their proximity and locations, such as uncontrolled construction, incineration and industrial works (e.g., cement industry) can also increase particulate matter in the air especially in urban areas.

The high level of PM is attributed to a combination of: (1) a high background from natural sources; (2) emission from mobile and fixed sources; (3) the large spatial scale of generation and spreading of particulate matter.

Lead, as an additive in petrol, has been removed from gasoline in many of the developing countries, however, still contributes a varying percentage in many urban areas. Lead concentration ranged from 0.04–9.47 μg/m^3 during the years (1992–1997) Hassanien et al. (2001). However, in recent study, Hassanien et al. (2006) found that lead concentration decreased to 0.28 μg/m^3 in urban locations in Cairo and the distribution of lead is characterised by relatively small scale spatial and temporal structures. Diesel engines also emit sulfur dioxides (SO_2) and fine particulate: the latter can penetrate easily into the respiratory system. Egypt emits 69 µg/m^3 of SO2 (compared to the WHO standard of 50 µg/m^3, World Bank, 1999).

TABLE 2. Ranges of average concentrations (µg/m^3) of pollutants for different regions based on a selection of urban data.

Region	Annual average concentration			Ozone (1-h max. concentration)
	PM_{10}	NO_2	SO_2	
Africa	40–150	35–65	10–100	120–300
Asia	35–220	20–75	6–65	100–250
Australia/New Zealand	28–127	11–28	3–17	120–310
Canada/United States	20–60	35–70	9–35	150–380
Europe	20–70	18–57	8–36	150–350
Latin America	30–129	30–82	40–70	200–600

It well illustrated from Table 2 that the highest concentrations of the “classical” indicators such as PM10 and sulfur dioxide are found in Africa, Asia and Latin America. The highest levels of secondary pollutants such as ozone and nitrogen dioxide are measured in Latin America and in some larger cities and urban airsheds in the developed countries.

These concentration levels significantly exceed WHO guidelines on air quality (WHO, 2005), which recommend the following ranges of values:

- $PM_{2.5}$: 10 µg/m^3 annual mean
- PM_{10}: 20 µg/m^3 annual mean
- O_3: 100 µg/m^3 for daily maximum 8-h mean
- NO_2: 40 µg/m^3 annual mean and
- SO_2: 20 µg/m^3 for 24-h mean

2. Definition and Concept of Exposure

Human exposure can be defined as “the event when a person comes into contact with a pollutant of a certain concentration during a certain period of time”. Conceptually, this occurs along the “environmental pathway” between concentration and dose, as follows.

Source → Emissions → Concentrations → Exposure → Dose → Health effects

“Exposure” should be distinguished from “concentration”, which is a quantitative expression of the amount of pollutant within a given environmental medium. High air pollution concentrations do not necessarily result in high exposures. For example, while air pollution concentrations may be very high near an emitting industrial facility, high exposures will occur only if people spend time near the facility. Exposure should also be differentiated from "dose", which refers to the amount of pollution that actually crosses one of the body boundaries. The dose will be defined by the characteristics of exposure (as defined above) as well as a wide range of factors specific to the pollutant (e.g. its solubility or pattern of deposition in the lung) and by physiological factors such as the person's level of activity, skin condition, etc.

Assessment of exposure to air pollution requires exposure estimates that are accurate, precise and biologically relevant, for the critical exposure period, and that quantify the range of exposure levels within the population under study.

Exposure to outdoor air pollution is influenced by the time spent outdoors, and is most important for people or populations who spend a substantial amount of time outdoors. When people spend only limited time outdoors, however, the direct contribution of outdoor air to personal exposure will generally be low, and most of the exposure to outdoor air pollution is actually encountered indirectly through the effect of outdoor air on indoor air (Janssen et al., 2005; Hassanien et al., 2006). This is particularly the case for non-reactive pollutants that penetrate easily from outdoors to indoors; for these pollutants time spent outdoors will have only a modest effect on total personal exposure. For some reactive pollutants such as ozone, or pollutants like coarse PM that penetrate poorly from outdoors to indoors for mechanical reasons, the indoor concentrations are much lower than those outdoors; for such pollutants the time spent outdoors can be a very important determining factor for exposure (Brauer and Brook, 1995).

3. Health and Environmental Implications of Toxic Chemicals

The hazards caused by toxic chemicals are devastatingly dangerous in the developing countries because:

1. People and governments are unaware of the inherent dangers of toxic chemicals.
2. The needed financial resources are either scarce or do not exist.
3. Facilities either for containing the wastes or for its destruction are not available.
4. Appropriate legal measures do not exist or, if they do, are either impossible or difficult to implement.
5. Environmental activists are either absent or too weak to stage public demonstration.
6. Expertise or skilled manpower is not available.

Ambient air is usually divided into two groups, the 'criteria' pollutants and 'other'. Criteria pollutants are those that are common air pollutants, found in relatively high concentrations. The 'other' group is made up of hazardous air pollutants and other specific substances that are found in trace concentrations are specific to a particular setting or activity and are monitored on a needs basis. In the case of some criteria pollutants, there are wide variations between concentration ranges due to meteorological factors and geography. Some methods are available to interpolate between monitoring stations and weight exposures according to population factors. If available, personal monitoring data would provide a much better indication on actual exposure, however this data is rarely available.

While the fundamental principles of risk assessment remain the same, different exposure assessment are available when assessing ambient air pollution from diffuse and point source regions or large areas, localised air pollution from point sources, and indoor air pollution such as may occur in the home or workplace. The levels of pollutants are compared with air quality standards that are usually health-based criteria, set either at levels below which adverse health effects are not expected to occur or at levels where the incidence of adverse health effects is considered acceptable. If the levels are found to exceed those in the standards, appropriate strategies and actions will need to be instigated to reduce the pollutants in the air shed.

4. Exposure and Risk Assessment

Exposure assessment is the most problematic area in the risk assessment process for air pollutants and is the source of most of the uncertainty in the estimation of risk. Some of the major difficulties are factors such as time and spatial variation of air pollutants and the fact that personal exposures are likely to rapidly vary and be affected by mobility and a range of other meteorological, physical and chemical processes. Risk assessment is a quantitative evaluation of information on potential health hazards of environmental contaminants and exerts of human exposure to these contaminants. The use of risk assessment as a tool in the decision-making process has become increasingly important over the last 2 decades for more specific judgment for the environmental situation and to address the chance of bad outcomes. Sound risk assessment should be based on the best scientific data and evidence available and the results of the exposure are combined with chemical-specific toxicity information to characterize potential risks. It has been accepted, for long, that urban and industrial activities give rise to some degree of contamination of soil, air and water which may lead to both direct and indirect impacts on the environment and human health.

The following section from this chapter contains an overview of some case studies carried out by author and others in developing country (Egypt). These studies represent risk estimates of air pollutants under different circumstances. The increasing pace of the development in Egypt has meant increased industrialization and increased demand for transportation. It is well documented how such industrialization and motorization, if not controlled, results in an increase in emissions and pollutant loading, which threaten people's health and overburdens the environment.

Cairo – Africa's largest city – continues to grow and its population density is steadily increasing: whereas in 1950 the city's population amounted to 2.41 million, in the year 2000 it had already approached the 10 million mark. (other figures estimate Cairo's population to be almost 20 million, including about 3 million daily commuters to the city.) With more than a third of Egypt's population residing in Cairo and with an average of more than 25,000 inhabitants per km² (in crowded downtown areas even up to 100,000 inhabitants per km²), Cairo is one of the densest agglomerations in the world. Air pollution in greater Cairo dangerously impairs the quality of life and has negative effects on business productivity. Cairo is a home of one third of Egypt's population, 60% of industries, 50% of electrical consumption and 48% of the country's motor vehicles (EEPP, 2004). Ambient monitoring provides information on local air quality. Therefore monitoring of their ambient levels is important not only in urban areas, but also in rural ones.

On the basis of available results, an extensive risk evaluation was made with respect to both health and environment. The purpose of this conclusive investigation was to establish the horizontal and vertical extent of the contamination in the environmental media and air in particular. In addition, one of the main objectives of this chapter is to explore the situation in the developing countries and investigate policies and regulations based on risk assessment methodologies in progress to cope up with this ever growing problem of the developing countries.

4.1. RISK ASSESSMENT OF EXPOSURE TO HEAVY METALS OF THREE DIFFERENT REGIONS IN EGYPT – CASE I

The case aimed to investigate the assessment of exposure of two population target groups at three different localities in Egypt. Human health risk assessment has been performed in relation to recreational activities on three different investigated areas two of them are mainly industrial-residential areas and the third is considered as a background one (rural area). To quantify health risk for carcinogenic and non-carcinogenic compounds, an exposure assessment model *(Risk*Assistant)* was applied using environmental pollution data as input parameters. Briefly, the computer software (*Risk*Assistant,* 1997) is a powerful set of tools and databases for estimating the health risk of various chemicals in the environment in particular settings. Default input parameters provided by the model are used, whenever possible, instead of a site-specific information.

Default parameters for calculating exposure have been extracted from the USEPA exposure factors handbook (Konz et al., 1989; USEPA, 1991). Estimates of human intake and exposure from heavy metals in environmental media (soil, air and plant) by the different age groups (1–6 year-children and adults) of the general population were based primarily on reported data for each site and using the specific exposure parameters. The intake is calculated according to the following equation:

$$\text{Intake (mg kg}^{-1}\text{ day}^{-1}\text{)} = \text{CC Q EF ED/BW}$$

where:
CC; concentration of the contaminant in the medium (soil, air, vegetable)
Q; ingested/inhaled quantity (mg day^{-1})
EF; frequency of exposure (day year^{-1})
ED; duration of exposure (year)
BW; body weight (kg)

TABLE 3. Mean, minimum and maximum concentrations of determined. metals in environmental media at investigated areas.

Element		Shoubra El-Khaima			Helwan			Monofia		
		Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Pb	Soil (mg kg^{-1} DW)	432.7	234	710	171.4	122	230	0.46	0.3	0.7
	Air (µg m^{-3})	2.06	1.1	3.7	1.72	1.4	2.2	0.023	0.011	0.035
	Vegetables (mg kg^{-1})	23.22	11	41	12.5	7.9	18	0.15	0.09	0.2
Cd	Soil (mg kg^{-1} DW)	23.22	11	41	12.11	7.5	18	0.14	0.1	0.3
	Air (µg m^{-3})	0.06	0.02	0.12	0.56	0.3	0.9	0.007	0.001	0.015
	Vegetables (mg kg^{-1})	7.33	2	11	1.97	1.2	3.1	0.04	0.02	0.06
Zn	Soil (mg kg^{-1} DW)	223.6	182	270	116.9	101	132	117	76	140
	Air (µg m^{-3})	0.51	0.4	0.7	0.78	0.6	0.92	0.046	0.007	0.12
	Vegetables (mg kg^{-1})	66.9	55	80	47.7	30	71	1.07	0.07	1.4
Ni	Soil (mg kg^{-1} DW)	7.47	2.7	15	8.14	5.5	11	0.24	0.11	0.42
	Air (µg m^{-3})	0.19	0.11	0.3	0.22	0.16	0.31	0.003	0.001	0.006
	Vegetables (mg kg^{-1})	2.07	1.2	3.1	0.32	0.21	0.41	0.02	0.11	0.04
Cu	Soil (mg kg^{-1} DW)	11.4	6	18	10.9	7.5	15	0.48	0.21	0.65
	Air (µg m^{-3})	0.22	0.11	0.3	0.19	0.11	0.31	0.003	0.001	0.009
	Vegetables (mg kg^{-1})	2.83	1.6	3.9	0.48	0.29	0.7	0.04	0.015	0.08

Metals concentration values were presented in Table 3; maximum concentration represents the worst-case scenario suggested by the USEPA exposure evaluation guidelines (Dura et al., 1995). Average Daily Doses (ADD) of total inhalation (dust and air) values are equal in both population groups for the examined metals (Table 4). In contrast, Lifetime Average Daily Doses (LADD) inhalation of air and dust are variable between adults and children groups as adults are exposed to higher lifetime average daily dose of air and dust through inhalation than children. On comparing ADD and LADD, it can been noticed that maximum values of these parameters for all metals are high in Shoubra El-Kheima than in Helwan and Monofia.

TABLE 4. Estimated average daily doses (ADD) and lifetime average daily doses (LADD) of metals by inhalation at the investigated sites.

	Adults				Children			
	ADD		LADD		ADD		LADD	
	Min	Max	Min	Max	Min	Max	Min	Max
Pb (μg m^{-3})								
Shoubra El-Khaima	38.1	116.2	13.93	42.64	38.1	116.2	7.58	23.18
Helwan	21.5	39.7	8.09	14.81	21.5	39.7	4.34	7.97
Monofia	0.068	0.177	0.027	0.073	0.068	0.177	0.014	0.037
Cd (μg m^{-3})								
Shoubra El-Khaima	1.73	6.52	0.623	2.37	1.73	6.52	0.342	1.29
Helwan	1.75	4.56	0.712	1.89	1.75	4.56	0.365	0.959
Monofia	0.017	0.076	0.006	0.031	0.017	0.076	0.003	0.016
Zn (μg m^{-3})								
Shoubra El-Khaima	28.7	42.8	10.38	15.5	28.7	42.8	5.69	8.49
Helwan	16.7	22.08	6.14	8.16	16.7	22.08	3.33	4.42
Monofia	11.7	21.7	4.17	7.8	11.7	21.7	2.30	4.29
Ni (μg m^{-3})								
Shoubra El-Khaima	0.634	2.9	0.258	1.12	0.634	2.9	0.132	0.592
Helwan	1.16	2.31	0.462	0.914	1.16	2.31	0.24	0.475
Monofia	0.019	0.076	0.007	0.029	0.019	0.076	0.004	0.015
Cu (μg m^{-3})								
Shoubra El-Khaima	1.14	3.36	0.439	1.29	1.14	3.36	0.232	0.683
Helwan	1.37	2.92	0.521	1.133	1.37	2.92	0.277	0.596
Monofia	0.034	0.118	0.012	0.045	0.034	0.118	0.007	0.024

The results of total exposures to these metals for both groups during their daily activities were used for computing the associated cancer risk Table 5. The total estimated cancer risk for adults group was the highest for all studied sites, due to long exposure duration. Results of Table 5 represent the minimum and maximum carcinogenic risk values expected for adults and children groups upon exposure to metals at different media. The estimated results showed that total carcinogenic risk is higher in Shoubra El-Khaima than other sites for adults and similar to the risk at Helwan for children. The results show that maximum risk from soil is greater than the corresponding from air at all sites for children and at Shoubra El-khaima only for adults. Potentially harmful effects of soil contamination by heavy metals are usually described as environmental hazard and environmental risk.

TABLE 5. Carcinogenic risk estimates from different media at examined sites.

		Sh. El-kheima		Helwan		Monofia	
	Medium	Min	Max	Min	Max	Min	Max
Adults	Air	4E-5	2E-4	5E-4	2E-3	2E-6	3E-5
	Soil	1E-3	4E-3	7E-4	2E-3	1E-5	3E-5
	Total	1E-3	4E-3	1E-3	3E-3	1E-5	6E-5
Children	Air	2E-5	1E-4	2E-4	7E-4	8E-7	1E-5
	Soil	6E-4	2E-3	4E-4	1E-3	5E-6	2E-5
	Total	6E-4	2E-3	7E-4	2E-3	6E-6	3E-5

TABLE 6. Non-carcinogenic risk estimates from different media at examined sites.

	Metal	Min	Max	Min	Max	Min	Max
Adults	Cd	3.4E-2	1.4E-1	2.3E-2	5.6E-2	3.2E-4	9.5E-4
	Zn	1.0E-3	1.5E-3	5.7E-4	8.6E-4	3.5E-4	6.4E-4
	Ni	2.5E-3	1.2E-3	3.9E-4	7.8E-4	1.4E-5	3.1E-5
Children	Cd	1.9E-1	7.3E-1	1.3E-1	3.1E-1	1.7E-3	5.2E-3
	Zn	5.4E-3	8.0E-3	3.0E-3	4.3E-3	2.0E-3	3.7E-3
	Ni	1.3E-3	6.5E-3	2.2E-3	4.5E-3	6.2E-5	1.7E-4

Concerning non-carcinogenic risk due to exposure to metals in studied environment Table 6, the estimated maximum risk was higher in children than in adults in all areas due to “hand-to-mouth” natural habit. Similarly to carcinogenic risk, the results reflected the highest risk in Shoubra El-Khaima than Helwan and Monofia. Moreover, cadmium had the highest risk compared to the other metals.

4.2. ESTIMATION OF INHALATION INTAKE OF METALS IN TRAFFIC AREA – CASE II

Exposure to atmospheric metal contaminants of indoor and outdoor microenvironments was examined. Ambient and indoor levels of Pb, Cd, Zn, Ni, Cr, Co, and V were investigated over 1 year in a residential area at the El-Nasr Road, which is one of the busiest and urbanized streets located at the eastern sector of Cairo. The concerned area is highly densely populated and characterized by commercial activities and huge number of running vehicles. Day, night and full-day composite air samples were collected individually over a 1-year period in 2003–2004.

The doses of contaminant metals that were inhaled by humans in outdoor/indoor environments were calculated using Microsoft® Excel workbook. The inhalation exposure dose (*IED*) in mg/kg/d due to the contact of children and adults with the contaminant media was estimated using the following equation (ATSDR, 1992; EPA, 1990):

$$IED = \frac{C \times IR \times EF}{BW}$$

where: $\underline{C}$; the concentration of the contaminant in μg/m^3, $\underline{IR}$; the inhalation rate in m^3/day, $\underline{EF}$; the exposure factor, and $\underline{BW}$; the body weight in kg.

As the exposure may occur on an irregular basis, *EF* can be calculated to average out the dose over the exposure intervals by multiplying the frequency of the exposure by its duration and divided by the time period over which the dose is to be averaged. However, some health effects may not depend on the average dose, but rather on the peak dose or some other measures of the dose rate. Many factors should be considered for the estimation of exposure risk.

$$EF = \frac{(days/week \times weeks/year \times years)}{years \times days/years}$$

TABLE 7. Input parameters for exposure estimation.

Parameter	Children	Adults	Reference
Inhalation rate (m^3/h)	0.62	0.92	enHealth (2002)
Exposure time (h/event)[a]	16 indoor 8 outdoor	20 indoor 4 outdoor	
Exposure frequency (event/year)	350	350	EPA (1990, 1991)
Exposure duration (year)[a]	6	30	
Body mass (kg)	24	70	EPA (1990, 1991)
Average time (day)[b]	2,190	10,950	

[a] Adjusted; [b] Calculated.

The concentration of the contaminant in the environmental medium is essential to determine the magnitude of the intake dose. The estimated exposure is significantly influenced by other factors including the duration and route of the exposure and intake rate. The input parameters required for the estimation of *IED* are summarized in Table 7. The absorption of all metal contaminants by children and adults through their lungs was assumed 100%.

The full-day, day-time, and night-time of the metals mean concentrations in outdoor and indoor atmosphere are summarized in Tables 8–11.

TABLE 8. Mean concentrations of heavy metals (μg/m^3) in the outdoor atmosphere of a residential area east Cairo.

Metal	Day time	Night time	Day/nightratio
Pb	0.2	0.11	1.82
Cd	0.004	0.005	0.8
Zn	0.063	0.12	0.53
Cr	0.02	0.004	5.0
Ni	0.006	0.011	0.55
Co	0.015	0.009	1.67
V	0.021	0.026	0.81

TABLE 9. Mean concentrations of heavy metals (μg/m^3) in the indoor atmosphere of a residential area east Cairo.

Metal	Day time	Night time	Day/nightratio
Pb	0.07	0.21	0.33
Cd	0.007	0.01	0.7
Zn	0.09	0.33	0.27
Cr	n.d.	n.d.	–
Ni	0.08	0.047	1.7
Co	0.16	0.01	1.6
V	0.034	0.042	0.81

TABLE 10. Full-day mean concentrations of heavy metals (μg/m^3) in the outdoor and indoor atmosphere of a residential area east Cairo.

Metal	Outdoor	Indoor
Pb	0.28	0.55
Cd	0.004	0.01
Zn	0.55	0.63
Cr	0.16	0.045
Ni	0.095	0.065
Co	0.016	0.24
V	0.039	0.046

TABLE 11. Mean indoor/outdoor ratios (I/O) of heavy metals in a residential area of east Cairo.

Metal	Full day	Day time	Night time
Pb	2.75	0.35	1.91
Cd	2.5	1.75	2
Zn	1.15	1.4	2.75
Cr	0.28	–	–
Ni	0.59	13.1	4.27
Co	15	1.07	1.11
V	1.64	1.62	1.62

TABLE 12. Inhalation Exposure Dose (*IED*) of the examined metals for children and adults.

	Concentration mg/m^3		*IED* of children mg/kg/day		*IED* of adults mg/kg/day	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Pb	5.5E-4	2.8E-4	2.2E-4	5.5E-5	1.4E-4	1.4E-5
Cd	0.1E-4	0.4E-5	4.0E-6	7.9E-7	2.5E-6	2.0E-7
Zn	6.3E-4	5.5E-4	2.5E-4	1.1E-4	1.6E-4	2.8E-5
Cr	4.5E-4	1.6E-4	1.8E-5	3.2E-5	1.1E-5	8.1E-6
Ni	6.5E-5	9.5E-5	2.6E-5	1.9E-5	1.6E-5	4.8E-6
Co	2.4E-4	1.6E-5	9.5E-5	3.2E-6	6.0E-5	8.1E-7
V	4.6E-5	3.9E-5	2.5E-5	7.7E-6	1.6E-5	2.0E-6

The intake by inhalation was computed from the concentrations of metals both in indoor and outdoor air (Table 12). For various metals, the *IED* values of children, either indoor or outdoor, were found to be higher than the corresponding values of adults. Moreover, indoor metal inhalation *IEDs* were higher than the corresponding outdoor ones, for both groups, except for chromium in children' group. Comparing the results of the present study with the atmospheric metal concentrations recorded in other countries (Table 13), the present metal concentrations were found to be much lower than those reported for China and similar to those found in Korea (Fang et al., 2005).

In all groups, the highest metal inhalation dose was that of Zn. Variability of the results in children and adults should be attributed both to the length of the exposure time and the body mass (see Table 7). On the other hand, increasing the inhalation dose in indoor environment coincides with the concentration trends of the metals examined.

TABLE 13. Mean concentrations of heavy metals (µg/m^3) in various countries.

	China[a]	Korea[a]	Jordan[b]	Argentina[c]		
		Full day		Day time	Night time	Day/night ratio
Pb	98.7	0.12	0.089	0.18	0.14	1.28
Cd	–	–	0.004	0.0006	0.0004	1.5
Zn	0.34	0.30	0.212	0.34	0.22	1.5
Cr	6.85	0.019	0.01	0.007	0.004	1.7
Ni	8.62	0.048	0.092	0.006	0.004	1.5
Co	–	–	0.011	–	–	–
V	–	–	0.013	–	–	–

[a] Fang et al., 2005; [b] Al-Momani et al., 2005; [c] Bilos et al., 2001.

The inhalation exposure doses calculated in the present study for Pb, Cd and Zn are far below the background exposure levels which have been estimated to be approximately 4.6E-4, 2.6E-4, and 1.9E-1 mg/kg/day for Pb, Cd, and Zn, respectively (CCRX, 1991). However, the estimated risk doses of the present study represent inhalation route only, as compared to the background levels that are valid for all exposure routes including inhalation.

In conclusion, Cairo residences are under considerable risk due to high atmospheric metal pollution. The exposure risk assessment of the present study can be used for screening purposes to estimate the risk of atmospheric metals absorbed by inhalation.

4.3. HAZARD ESTIMATION OF H_2S AND NH_3 EXPOSURE – CASE III

This study was conducted at the western district of Giza region (Cairo, Egypt), where there are many scattered markets for vegetables, meats, fish, and poultry. At the end of the day, traders get rid of their market waste dumping them to the nearby running stream. The surrounding area is, therefore, exposed to both NH_3 and H_2S produced as a result of microbial action in organic waste containing sulfate ions and nitrogen. To monitor H_2S and NH_3, three sites were chosen in the Giza region (Sites 1, 2, and 3) and another one in a new residential area.

The objective of this case was to: (1) determine the gaseous emission levels from anaerobic degradation of organic waste (animal residues, vegetables, fruits, and fishes) accumulated in a narrow stream crossing the investigated area, and their impact on the air quality of the residential area; (2) assess whether population residents of that area at potential risk due to inhalation of the emitted gases. Monthly and annual mean concentrations of atmospheric NH_3 at the sites of measurement are presented in Table 14. It shows that the monthly mean concentrations of NH_3 ranged from 63 to 224, 71 to 220, and 71 to 142 μg/m^3 at Sites 1, 2, and 3, respectively. The corresponding values recorded at Site 4 (control) were 23 and 9 μg/m^3.

TABLE 14. Monthly mean concentrations (± SD) of H_2S and NH_3 (μg/m^3).

	Site 1		Site 2		Site 3		Site 4	
Month	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3
December 2004	155 ± 18	123 ± 18	134 ± 28	113 ± 25	109 ± 47	77 ± 20	13 ± 5	10 ± 3
January	138 ± 27	101 ± 28	105 ± 23	71 ± 21	96 ± 21	81 ± 8	12 ± 2	9 ± 4
February	133 ± 27	93 ± 18	105 ± 10	97 ± 9	93 ± 13	86 ± 25	9 ± 3	13 ± 2
March	102 ± 17	80 ± 14	101 ± 14	92 ± 19	88 ± 25	71 ± 13	12 ± 2	11 ± 2
April	91 ± 13	75 ± 13	93 ± 17	81 ± 19	90 ± 16	78 ± 13	11 ± 2	13 ± 4
May	91 ± 15	74 ± 16	102 ± 43	105 ± 51	92 ± 23	79 ± 22	17 ± 3	14 ± 3
June	242 ± 52	178 ± 30	265 ± 43	159 ± 41	191 ± 35	140 ± 47	12 ± 6	22 ± 7
July	252 ± 41	192 ± 39	239 ± 35	184 ± 26	218 ± 40	142 ± 38	15 ± 5	21 ± 4
August	261 ± 47	224 ± 57	288 ± 48	220 ± 45	215 ± 26	136 ± 18	15 ± 3	23 ± 6
September	112 ± 9	90 ± 11	101 ± 22	98 ± 39	100 ± 13	78 ± 20	11 ± 1	13 ± 3
October	84 ± 18	63 ± 20	92 ± 15	80 ± 20	93 ± 17	83 ± 19	11 ± 4	14 ± 3
November 2005	90 ± 12	84 ± 19	93 ± 13	78 ± 13	90 ± 11	95 ± 17	11 ± 3	14 ± 1
Annual mean ± SD	146 ± 74	115 ± 57	143 ± 81	116 ± 48	123 ± 58	95 ± 29	12 ± 2	15 ± 5

Table 15 shows that the highest concentrations of NH_3 were recorded in the summer season; they were 1.9–2.5 times larger than the concentrations recorded in other seasons. One-way ANOVA for the seasonal effects shows that there is a significant difference between summer and other seasons mean concentrations. Similar to NH_3, Table 15 shows that H_2S concentration in summer was 1.8–2.8 times larger than those recorded in other seasons. Adjusted inhalation concentration in outdoor and hazard quotient (HQ) for the groups of both adults and children are shown in Table 16. Potential hazard estimates of both NH_3 and H_2S, developed by *Risk*Assistant* model, reflected higher annual inhalation for adults than children groups and a consequent higher HQ to both population groups.

TABLE 15. Seasonal concentrations (± SD) of H_2S and NH_3 (µg/m^3) at the sites studied.

	Site 1		Site 2		Site 3		Site 4	
	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3
Winter	142 ± 12	106 ± 16	115 ± 17	94 ± 21	99 ± 9	81 ± 5	11 ± 2	11 ± 2
Spring	95 ± 7	76 ± 3	99 ± 5	96 ± 8	90 ± 2	76 ± 5	13 ± 2	13 ± 2
Summer	252 ± 10	197 ± 25	264 ± 25	188 ± 31	208 ± 15	139 ± 3	14 ± 2	22 ± 1
Autumn	95 ± 15	79 ± 14	95 ± 5	85 ± 11	94 ± 5	85 ± 8	11 ± 0.0	13 ± 1

TABLE 16. Assessment the exposure of adults and children due to annual concentrations of H_2S and NH_3 at the investigated area.

	H_2S				NH_3			
	Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
Adults								
AC (µg/m^3)	11.04	10.82	9.31	0.908	8.75	8.77	7.19	1.14
Children								
AC (µg/m^3)	8.68	8.51	7.32	0.714	6.84	6.90	5.65	0.89
H Q	146	143	123	12	1.15	1.16	1.0	0.15

In this case, daily concentrations were also higher than that given in the WHO air quality guideline for H_2S (150 µg/m^3; WHO, 2000) with about 36%, 27%, and 25% for the days of measurements at Sites 1, 2, and 3, respectively. This high level of H_2S was produced due to bacterial breakdown of plant and animal waste in stagnant water with low oxygen content. To avoid odour annoyance, a 30-min average ambient air concentration not exceeding 7 µg/m^3 is recommended (WHO, 2000). HQ of a non-carcinogenic toxic agent compares the expected exposure to that agent to the exposure at which no adverse health effects are likely to occur. In case of inhalation exposure, the inhaled concentration is compared to the agent's reference concentration (RfC). Reference concentrations of H_2S and NH_3 are 0.001 and 0.1 mg/m^3, respectively (CIIT, 1983; USEPA, 1999). The results reflect the increase of adjusted concentration of H_2S and NH_3 with the increase of their concentrations at the areas investigated. Under the conditions applied for the exposure assessment (e.g., concentration, age, exposure frequency, and inhalation rate), hazard quotient were greatly higher than 1.0, except for NH_3 at Site 3 and 4, suggesting their high contribution to inhalation exposure risk for both population groups. However, exposure of children to air pollution, in contrast to that of adults, is special concern because of their undeveloped immune system and lung which raise the possibility of various intricate.

5. Conclusions

On the basis of the available results reported in the present chapter, the following remarks can be drawn:

1. The present data established both of the horizontal and vertical extent of contamination in the environmental media and air in particular.
2. Cairo residences as an example of developing countries population are under considerable risk due to high atmospheric metal pollution.
3. Exposure risk assessment results can be used for screening purposes to estimate risk resulting from atmospheric metals through inhalation route.
4. The results present the first attempt to assess exposure hazards of H_2S and NH_3 in Egypt, as the few previous studies have dealt with the risk of metal pollution. The data presented may contribute to evaluate the relative risk of various harmful environmental pollutants.

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INHALATION INTAKE ASSESSMENT OF AIR POLLUTANTS EXPOSURE OVER CAIRO, EGYPT

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Abstract. Estimation of the exposure to air pollutants is more relevant than the ambient air quality since it gives a better indication of health risk. The primary purpose of this study is to quantify the inhalation exposure risk due to atmospheric heavy metals pollutants emitted from different activities in the city on population, explores the main factors influence differences in inhalation intake of the concerned population groups and finally suggest broad strategies for reducing inhalation intake burden. Samples of ambient urban air were collected during June–August 2007 from eight sampling sites representing different activities and land use. Measured elements in airborne particulates were chromium, cobalt, nickel; iron, manganese, copper, zinc and vanadium. Different techniques of AAS were used according to the analytical conditions for each element. The atmospheric mean concentrations (µg/m^3) of the measured metals at different sites were found to be in the range of: Cr (0.004–0.032), Co (0.0001–0.046), V (0.007–0.1), Mn (0.035–0.283), Fe (1.702–9.547) Ni (0.002–0.042), Cu (0.006–0.17), and Zn (0.023–2.6). Spatial differences between collection sites were clearly noted reflecting the characteristics and different activities of each site. In this study, outdoor population were divided into two categories, normal particular population viz. outdoor workers e.g. traffic constables and casual outdoor workers like watchmen, roadside shopkeepers etc. Using environmental concentration data presently available from Cairo (especially for air), the paper will compute human exposure through inhalation intake route. The total estimated inhalation intake based on average concentration of atmospheric metals in Rod El-Farag and El-Tebeen sites were the highest for almost all metals giving excellent relation between concentrations and intake values for the investigated population. The current study may allow concluding that exposure to chemical emissions from different anthropogenic activities is related to risk.

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Keywords: toxic metals, air, inhalation dose, intake assessment, population

1. Introduction

Anthropogenic air pollution from sources like motor vehicles and industries continues to be serious environmental problems such as the restriction of atmospheric visibility, while their toxicity may present health problems to humans at certain concentrations (Milford and Davidson, 1985). Heavy metals emissions from factories or car exhausts have been implicated in a variety of cardio-respiratory problems associated with exposure to urban air pollution. Its seriousness is due to the fact that elevated air pollutant levels from these anthropogenic sources tend to occur in environments where serious harm to human health and welfare is more likely, namely the more densely populated urban areas. The health impacts of air pollution depend on the sensitivity and the exposure level of the susceptible population to the pollutant. The largest health impacts in most developing country cities result from exposure to fine particulate pollution (Gwilliam et al., 2004; Hassanien, 2001).

A series of environmental studies identified air pollution as the most critical environmental problem in Cairo with particulate matter and toxic metals as the greatest health risks in Cairo's air (IARC, 1990; WHO, 2005; EPA, 1984).Toxic substances, which are released constantly into air by many types of industrial and urban activities, until now have never been quantified in Egypt. Evidence as to the health risk posed by contacting with of such pollution is limited. The multiple sources of air pollution and the heavy load of pollutants are consequence of accelerated socio-economic growth Egypt witnessed over the past three decades. Air pollution increases with the growing-economic development in Egypt (Hassanien et al., 2006).

Heavy pollutants load in Egypt is attributed to a multiple sources of air pollution including vehicle emissions, industrial and manufacturing facilities, municipal waste sites and incinerators. The number of vehicles increases over last decades and they already exceeded 3.5 million vehicles in 2005, or 10% annually. Industrial zones, especially in Greater Cairo (Helwan, Shoubra El-Khaima and El-Tebeen) and numerous other areas abound in various industries, in addition to widespread small industries within the populous mass. Moreover, Cairo Air Improvement Project conducted in 2001 concluded that solid municipal waste burning in the open air accounts for 36% of the total annual load of pollution with suspended chest particles in Greater Cairo air. Exhaust accounts for 26%, whereas industrial emissions and agriculture waste open burning account for 32% and 6% respectively (EEPP, 2004a, b).

Several toxic metals, including arsenic, cadmium, lead, zinc, antimony and their compounds are associated with fine particulate matter in ambient air (EPA, 1996). This is important from a public health perspective since these fine particles are respirable and can be transported over very long distances. Heavy metals such as iron (Fe), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), manganese (Mn), and copper (Cu) exist in both coarse and fine fractions in ambient air (EPA, 1998). Metals such as arsenic (As), cadmium (Cd), lead (Pb), antimony (Sb), selenium (Se), and zinc (Zn) enrich the fine fraction of particulate matter (Finlayson-Pitts and Pitts, 1986).

Potential health effects caused by inhaling contaminants range from relatively minor impacts, such as respiratory irritation, headaches and cough, to more serious health impacts, including asthma, cancer and advanced mortality in those already suffering serious illness (MFE, 2002).

Assessment of human inhalation intake from airborne toxic metals is an important target. Large segments of Egyptian population have been, and are now being exposed to toxic chemicals from all media and through all routes of exposure (inhalation, ingestion, and dermal absorption) (LIFE, 2005). The connection between sources of pollution and their health effects is based on the transformation into suitably averaged concentration (mass of pollutant per unit volume of air). The link between concentration and the health effects follows from accounting for the direct inhalation (mass of the original pollutant per volume of air inhaled by the individual). The study was carried out for a particular population subgroup, viz. outdoor workers like traffic constables, shopkeepers, and watchmen. It was envisaged that the worst daily exposure to air pollution is for low and middle income population residing with an outdoor occupation who exposure to both the worst outdoor air quality due to vehicular and industrial pollution and also the worst indoor air quality due to low income level and poor living conditions. This study is a new research field which has not been attempted before in Egypt. The objectives of the study are to determine inhalation intake exposure of population to heavy metals and investigate the correlation with their ambient metal concentrations.

2. Materials and Methods

The investigated area Cairo, the capital of Egypt, is the largest city in the Middle East and one of the world's most densely populated cities, with one of the lowest provisions of road space per capita and dramatic growth in the number of private vehicles. The present study was conducted at different district areas characterized by different anthropogenic activities within the Greater Cairo. These areas were chosen carefully to represent various industrial, urban, commercial and residential activities. The areas investigated are scattered along Cairo city and characterized also by huge number of running vehicles. The characters of the selected sites are presented in Table 1.

TABLE 1. Character of sites over greater Cairo.

No.	Site	Main activity
1	Rod El-Farag	Residential
2	Torra	Industrial
3	Tebbin	Industrial
4	Ramsis	Residential
5	Qaluib	Traffic
6	Maadi	Traffic
7	Helwan	Rural
8	Embaba	Residential

3. Sampling and Analysis

Determination of metals content in airborne particulate matter involves three major steps. The first is the collection of suspended particulate matter onto appropriate filter papers, the next is the preparation of the filter sample for analysis and the last is the instrumental analysis of the filter contents to determine the chemical composition of the particulate matter. 24-h composite ambient urban air samples were collected individually during June–August 2007. Ambient atmosphere sampling was carried out at the investigated sites using a calibrated vacuum pump equipped with a cellulose membrane filter of 47 mm diameter in an open-faced holder. The efficiency of filter was about 100% for fine particles of 0.1 µm size (Harrison and Perry, 1986). During the monitoring program, a total of 12 samples were collected from each site to cover the fluctuations due to traffic flow and weather conditions. Before and after sample collection, the filters were conditioned in a dissector for 24 h. Filters were weighed before and after the sampling period and the amount of the collected particulate matter was determined as the gain in sample mass. The filters were handled in a dust-free room at 20°C ± 4°C. The air concentration of particulate matter was evaluated using the volume of samples and expressed in $\mu g/m^3$.

The samples of ambient urban air samples were digested in a mixture of HNO_3, HCl, and $HClO_4$. Having obtained a colourless solution by heating, the samples were evaporated to dryness and the residue was completed to a known volume of 0.25% HNO_3 (Tripathi et al., 1997; EPA, 1999; Hassanien et al., 2006). The metal contents were measured using atomic absorption spectrophotometer [Shimadzu AA-670, flame AAS (FAAS) and Varian AA-1275 equipped with GTA-95 atomizer techniques].

4. Quality Assurance

Two sample blanks were analyzed together with each batch of samples. Concentrations of the metal in the blanks were below the detection limits in all analysis. A spiked blank was analyzed during each analysis to ensure day-to-day reproducibility. Each standard and sample was measured in duplicate, and the sample was re-analyzed if the relative standard deviation of the two measurements was higher than 5%. Coefficients of variations of the three replicates of the samples were generally less than 10% and the mean was used as the representative value for the sample. In the present study, all laboratory tools used in sample collection, ashing, analysis, and storage were soaked in 10% HNO_3 for several days and then rinsed thoroughly with distilled and double distilled water, respectively, before use. Laboratory check samples were prepared from unexposed mineralized filters with standard addition of elements. Furthermore, a standard reference material (SRM 1648) from NITS (USA) has been used to validate the analysis.

5. Assessment the Exposure

In this section, an attempt has been done to estimate exposure of Egyptian citizens for eight pollutants (toxic metals) in air. Distribution associated with inhalation rate, body weight, residency duration, time spent outdoors as well as the total hours away from home has been characterized by numerous investigators (Silvers et al., 1994; Funk et al., 1998; Hassanien et al., 1999; Hassanien, 2001; EPA, 1984). The doses of contaminant metals that were inhaled by humans in outdoor environment were calculated using Microsoft® Excel workbook (Hassanien et al., 2006). Consider the air pollution health effects paradigm illustrated in Figure 1. The system begins with sources that emit

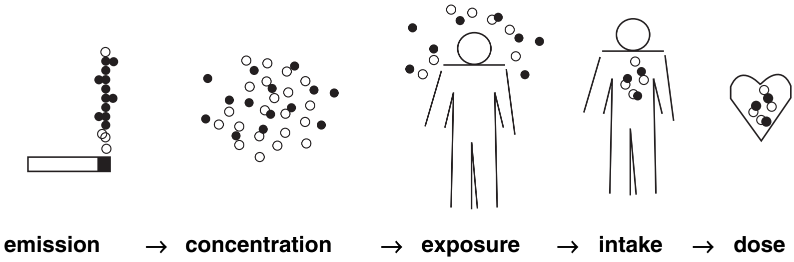

Figure 1. Paradigm of air pollution health effect.

pollutants into air. The pollutants are transported, dispersed, and transformed to yield concentrations that vary in time and space. People are exposed to pollutants when they encounter these concentration fields. Intake represents the inhalation of contaminants owing to their presence in the breathed air.

Adults inhalation exposure dose (IED) in mg/kg/day due to inhalation of ambient air was estimated using the equation reported by Hassanien et al. (2006) according to ATSDR (1992) and EPA (1990):

$$IED = \frac{C \times IR \times EF}{BW}$$

where C is the concentration of the contaminant in μg/m^3, IR is the inhalation rate in m^3/d, EF is the exposure factor, and BW is the body weight in kg.

As the exposure may occur on an irregular basis, EF can be calculated to average out the dose over the exposure intervals by multiplying the frequency of the exposure by its duration and divided by the time period over which the dose is to be averaged:

However, some health effects may not depend on the average dose, but rather on the peak dose or some other measures of the dose rate. Many factors should be considered for the estimation of exposure risk.

$$\text{EF} = \frac{(\text{days/week} \times \text{weeks/year} \times \text{years})}{\text{years} \times \text{days/years}}$$

The concentration of the contaminant in the environmental medium is essential to determine the magnitude of the intake dose. The estimated exposure is significantly influenced by other factors including the duration and route of the exposure and intake rate. The input parameters required for the estimation of IED are summarized in Table 2. The pulmonary absorption of all metal contaminants by adults was assumed to be 100%.

TABLE 2. Input parameters for exposure estimation.

Parameter	Values	Reference
Inhalation rate (m^3/h)	0.92	enHealth (2002)
Exposure time (h/event)[a]	[8] High (outdoor workers) [3] Normal (Normal)	
Exposure frequency (event/year)	350	EPA (1990, 1991)
Exposure duration (year)[a]	30	
Body mass (kg)	70	EPA (1990, 1991)
Average time (day)[b]	10,950	

[a] Adjusted.

[b] Calculated.

6. Results and Discussion

In recent years, air pollution is one of the most obvious and important environmental problems in Cairo City. Cairo, the capital of Egypt has approximately 17 million people. An evaluation of the concentrations of trace elements in Cairo ambient air is extremely important for proper assessment of the hazard associated with their intake. As a first attempted in Egypt, a multi-elemental analysis of air was carried out in this study. Consequently, this paper was performed to estimate human exposures by using environmental concentration of presently available data for air and points out research and monitoring needs. The analysis in this study demonstrated the significant variability in air pollution concentrations found in the investigated areas, with evidence that local activity patterns played an important role.

Table 3 shows the concentrations of different metals at the investigated sites over Cairo. Spatial differences were found reflecting the characters and land use of the concerned sites. the concentration of chromium was found in the range 0.002–0.032 µg/ m^3 (2–32 ng/m^3) lower than that reported concentrations in the European Union Member States where the concentration of Cr was found in a survey as follows: remote areas 0–3 ng/m^3; urban areas: 4–70 ng/m^3, and industrial areas 5–200 ng/m^3 (EPA, 1984; Lahmann et al., 1986).

The present data in Table 3 illustrated that nickel concentration in Cairo was lower (0.002–0.042 µg/m^3) than the reported levels in northern Norway, where a level of about 1 to 64 ng/m^3 was recorded in areas with different activities (Norseth, 1994; Sivertsen et al., 1991). Similarly, the present data was lower than concentrations recorded for Ni, with a maximum of 45.1 ng/m^3 and a minimum of 3.49 ng/m^3 in Spata (traffic area) Greece (Ch. Vassilakos et al., 2007). Current results are in agreement with the concentrations of 18–42 ng/m^3 which recorded in eight United States cities and with the ranges of 10–50 ng/m^3 and 9–60 ng/m^3 have been reported in European cities. Meanwhile, lower than values (110–180 ng/m^3) have been reported from heavily industrialized areas in Europe (Bennett, 1994).

For copper and zinc the data presented higher values for zinc compared with the data found by Ibrahiem et al. (2005) in similar sites. On the other hand, copper recorded lower values than the data reported in the previous study. Moreover, cobalt and vanadium values ranged from (0.001–0.046) and (0.007–0.1) µg/m^3, respectively reporting higher values for cobalt than the results found by Hassanien et al. (2006) and lower than the same study data for the case of vanadium. It might be explained the existence of the main contributors to trace elements in Cairo are street dust and vehicles exhausts (Hassanien et al., 2001). The reported concentrations for the examined elements, in the current study, were found to be higher than those reported by Hassanien and Shakour (1999) in suburban resort area (Hurghada, Egypt).

TABLE 3. Metal concentrations (μg/m^3) in different sites over Cairo.

Site[a]	1	2	3	4	5	6	7	8
Vanadium average (μg/m^3)	0.068	0.022	0.038	0.025	0.020	0.021	0.026	0.024
Max	0.101	0.037	0.049	0.063	0.056	0.028	0.042	0.040
Min	0.049	0.004	0.026	0.1e−5	0.006	0.013	0.015	0.016
SD	0.020	0.012	0.012	0.020	0.018	0.007	0.014	0.011
Chromium average (μg/m^3)	0.013	0.012	0.019	0.010	0.007	0.007	0.016	0.007
Max	0.017	0.016	0.032	0.017	0.011	0.012	0.030	0.008
Min	0.008	0.008	0.011	0.006	0.004	0.005	0.005	0.006
SD	0.003	0.003	0.011	0..004	0.003	0.003	0.013	0.001
Manganese average (μg/m^3)	0.193	0.065	0.163	0.066	0.058	0.055	0.074	0.053
Max	0.283	0.109	0.246	0.120	0.097	0.072	0.115	0.068
Min	0.115	0.047	0.098	0.041	0.035	0.038	0.041	0.045
SD	0.053	0.022	0.075	0.026	0.021	0.014	0.038	0.011
Iron average (μg/m^3)	4.559	3.634	6.211	3.377	2.858	2.894	3.003	2.411
Max	7.579	6.416	9.547	0.629	5.110	3.980	4.696	3.035
Min	3.271	2.655	4.162	1.978	1.702	2.083	1.833	2.025
SD	1.480	1.338	2.914	1.411	1.132	0.836	1.502	0.437
Cobalt average (μg/m^3)	0.023	0.022	0.028	0.017	0.016	0.012	0.017	0.011
Max	0.031	0.034	0.046	0.041	0.034	0.014	0.027	0.013
Min	0.017	0.011	0.012	0.010	0.007	0.008	0.013	0.001
SD	0.005	0.007	0.017	0.010	0.009	0.003	0.005	0.001
Nickel average (μg/m^3)	0.030	0.011	0.016	0.013	0.010	0.006	0.008	0.011
Max	0.042	0.018	0.025	0.024	0.031	0.008	0.013	0.016
Min	0.022	0.006	0.010	0.006	0.003	0.002	0.006	0.005
SD	0.008	0.004	0.009	0.006	0.009	0.003	0.004	0.005
Copper average (μg/m^3)	0.061	0.041	0.032	0.043	0.018	0.114	0.057	0.139
Max	0.100	0.057	0.053	0.090	0.047	0.123	0.064	0.167
Min	0.036	0.026	0.019	0.028	0.006	0.105	0.049	0.097
SD	0.026	0.012	0.019	0.021	0.014	0.009	0.008	0.031
Zinc average (μg/m^3)	1.810	0.309	0.682	0.389	0.047	3.806	0.378	0.195
Max	2.591	0.577	0.823	0.685	0.101	6.068	0.547	0.347
Min	0.813	0.126	0.484	0.163	0.023	1.115	0.220	0.097
SD	0.692	0.168	0.176	0.173	0.027	2.408	0.163	0.112

[a] 1 – Rod El-Farag, 2 – Torra, 3 – Tebbin, 4 – Ramsis, 5 – Qaluib, 6 – Maadi, 7 – Helwan, 8 – Embaba.

TABLE 4. Assessment of inhalation Dose mg/kg/day for the investigated population.

		Fe		Mn	
		Normal	High	Normal	High
Rod El-Farag	Min	1.10e−4	2.80e−4	3.73e−6	9.94e−6
	Max	1.88e−4	5.01e−4	9.07e−6	2.42e−5
	Average	1.48e−4	3.94e−4	6.16e−6	1.64e−5
Torra	Min	8.60e−5	2.30e−4	1.52e−6	4.06e−6
	Max	2.07e−4	5.53e−4	3.56e−6	9.51e−6
	Average	1.17e−4	3.112-4	2.11e−6	5.62e−6
Tebeein	Min	1.30e−4	3.60e−4	3.17e−6	8.47e−6
	Max	3.09e−4	8.25e−4	8.10e−6	2.16e−5
	Average	2.01e−4	5.36e−4	5.18e−6	1.38e−5
Ramsies	Min	6.40e−5	1.70e−4	1.33e−6	3.54e−6
	Max	2.04e−5	5.44e−5	3.89e−6	1.04e−5
	Average	1.09e−4	2.92e−4	2.14e−6	5.70e−6
Qaluib	Min	5.50e−5	1.50e−4	1.13e−6	3.02e−6
	Max	1.66e−4	4.42e−4	3.14e−6	8.38e−6
	Average	9.27e−5	2.47e−4	1.80e−6	5.01e−6
Maadai	Min	6.70e−5	1.80e−4	1.23e−6	3.28e−6
	Max	1.29e−4	3.44e−4	2.33e−6	6.2e−6
	Average	9.36e−5	2.50e−4	1.78e−6	4.75e−6
Helwan	Min	5.90e−5	1.60e−4	1.33e−6	3.54e−6
	Max	1.52e−4	4.06e−4	3.89e−6	1.04e−5
	Average	9.72e−5	2.59e−4	2.40e−6	6.39e−6
Embaba	Min	6.50e−5	1.70e−4	1.46e−6	3.89e−6
	Max	9.82e−5	2.62e−4	2.20e−6	5.80e−6
	Average	7.78e−5	2.07e−4	1.72e−6	4.58e−6

		V		Cr	
		Normal	High	Normal	High
Rod El-Farag	Min	1..62e−6	4.32e−6	2.69e−7	7.17e−7
	Max	3.24e−6	8.64e−6	5.51e−7	1.47e−6
	Average	2.20e−6	5.88e−6	4.05e−7	1.08e−6
Torra	Min	9.72e−8	2.59e−7	2.75e−7	7.34e−7
	Max	9.72e−7	2.59e−6	5.18e−7	1.38e−6
	Average	6.80e−7	1.81e−6	1.04e−6	1.00e−6
Tebeein	Min	6.48e−7	1.73e−6	3.56e−7	9.51e−7
	Max	1.62e−6	4.32e−6	1.04e−6	2.76e−6
	Average	1.23e−6	3.28e−6	6.06e−7	1.62e−6

TABLE 4 (continued)

Ramsies	Min	3.24e−8	8.64e−8	1.80e−7	5.01e−7
	Max	1.94e−6	5.18e−6	5.51e−7	1.47e−6
	Average	8.10e−7	2.16e−6	3.11e−7	8.30e−7
Qaluib	Min	1.62e−7	4.32e−7	1.26e−7	3.37e−7
	Max	1.62e−6	4.32e−6	3.56e−7	9.51e−7
	Average	6.48e−7	1.73e−6	2.11e−7	5.62e−7
Maadai	Min	3.24e−7	8.64e−7	1.52e−7	4.06e−7
	Max	9.72e−7	2.59e−6	3.89e−7	1.04e−6
	Average	6.80e−7	1.81e−6	2.36e−7	6.31e−7
Helwan	Min	6.48e−7	1.73e−6	1.75e−7	4.67e−7
	Max	1.30e−6	3.46e−6	9.72e−7	2.59e−6
	Average	8.42e−7	2.25e−6	5.28e−7	1.41e−6
Embaba	Min	3.24e−7	8.64e−7	1.85e−7	4.92e−7
	Max	6.98e−7	1.73e−6	2.59e−7	7.17e−7
	Average	7.78e−7	2.07e−6	2.40e−7	6.39e−7

The present study attempted to quantify human inhalation intake dose resulting from exposure to the examined metals at the concentrations reported. It is more convenient to calculate the absorbed dose as amount of intake per unit body mass and unit time (mg/kg/day) (Paustenbach, 2000). Variability in the current risk prediction may originate from either the human characteristics (e.g., age or body mass) and human behavior (e.g., location and activity patterns). Inhalation rate, as a factor used, was reported to be related to age specific data (Dura et al., 1995; Funk et al., 1998). It was assumed that exposure level, duration and frequency do not change during the lifetime if the human activities remain the same. Due to the small metal mass inhaled, 100% bioavailability is assumed.

The intake as shown in Table 4 by inhalation was computed from air concentration of metals, The IED values found to varied spatially and have elevated trend with increasing the concentrations. The data presented in Table 4 illustrated clearly the wide spectrum of inhalation dose for the investigated metals over different sites over Cairo for both population groups. Great care was paid to numerical assumptions to achieve the lowest possible uncertainty of dose estimation. Despite that direct measurement of the exposure of population is useful to provide the best exposure data, default exposure factor data are often required (Langely, 1993).

To discuses some examples from the measured metals, in case of our specific scenarios as shown in Table 4, the amount of airborne chromium entering the respiratory tract is in the rang 0.01–1 and 0.02–3 ng per outdoor exposure time for (Normal) and (High) outdoor workers in Teebin site (industrial area), respectively.

Individual uptake may vary depending on concomitant exposure to other relevant factors, e.g. tobacco smoking, and on the distribution of the particle sizes in the inhaled aerosol. Owing to the variation in particle size and solubility between nickel compounds, no general statements can be made on the retention or absorption of nickel in the respiratory tract (Oberdörster, 1992). A total deposition of about 50% of the inhaled dose was estimated for particles with diameter of 2.0 μm, while deposition was about 10% for those of 0.5 μm. For larger particles, more than 50% of the deposited dose was in the nasopharyngeal part of the respiratory tract as against less than 10% for the smaller particles.

In conclusion, to reduce the health and environmental effects of air pollution and ensure that air is clean for future generations, it is important to reduce emissions of pollutants into the air we breathe. In fact, Egypt has paid special attention for monitoring and reducing such emissions through concerted efforts under taken at both national and international levels alike. Environmental action in Egypt encounters numerous challenges that made it imperative to apply traditional and non-traditional techniques to bridge the gap between the quality of life Egyptians aspire to and that which they really get as a result of ongoing pressures affecting their environment.

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WATER QUALITY ASSESSMENT AND CONTROL IN BULGARIA

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Abstract. An analysis of the Bulgarian legislation in the field of water and wastewater management harmonized with the European Union's one during the last decade, regarding laws, directives, standards, etc. and its implementation is made. The results of the analysis show that water and wastewater quality assessment and control in Bulgaria are performed according to the legislation. Some modifications of the Bulgarian legislation are still needed. It is emphasized on that permanently water and wastewater quality assessment and control with modern tools are essential in the process of water/water resources management and for health and environmental risk assessment. They will provide not only environment and human beings protection but also technological means evaluation and improvement of the environment. People should start being more responsible to this point.

Keywords: water quality assessment, waste water treatment, risk assessment

1. Introduction

Life is water phenomena and that makes water extremely essential for it. Nevertheless most of the planet, about 72% is covered with water only less than 3% is not salty. Most of the fresh water is under the form of continental ice and groundwater. Bulgaria has not got abundant water resources compared to most of the other European countries. The water quantity formed within the country's territory, depending on precipitation varies between 9 and 24 billion cubic meters annually. The average annual amount per citizen is roughly 2,300 to 2,500 m^3/year, but only 800 to 1,000 m^3 are usable. Due to the fact that in normal conditions water is liquid it distributes itself almost everywhere, managing to get through almost all kind of barriers. That leads to one very

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outstanding fact – contaminants in water can spread really fast and even small quantities of them can affect large areas. Natural processes like volcano eruption, earthquakes, ore deposits, etc. could cause pollution, but mainly it is caused by human activities. The scarce water resources, their pollution and the trend of rising water consumption lead to higher and higher lack of water. All that originates health risk for people and animals and the environment. To control this risk and try to minimize it as much as possible, a proper water risk assessment and management should be performed. Risk assessment and management are based on precise analysis of all water quality parameters, their impartial assessment and strict systematic control, which become more and more crucial in nowadays world. All of them apply the legislation and use different standards for sampling.

2. Legislation Gives Assistance in Water Quality Assessment and Management

During the past 10 years in Bulgaria the role of the state in the water policy has been changing from governing to regulative. Meanwhile the country was preparing for becoming European Union member. The first step was to harmonize the legislation. In the field of water policy it included acceptance of the Water Framework Directive, passing of a new Water Law and 14 Regulations supporting its implementation till December 2007, transferring the requirements of the relative European Union's Directives for water protection and water quality standards. New Law for Water Management was elaborated, discussed and approved in 2005 according to the National Strategy for Management of Water Sector Development till 2015, which was accepted in 2004. There are also some events still to come and they are publishing of River Basin Management Plans with final version of water body ecological status classification to **2009**, adoption of water pricing policy based on environmental objectives to **2010**, repealing some older directives to **2013**, achieving "good water status" to **2015**. The legislation gives the base, which the executive authorities step on. They can be separated basically to two groups.

National level (NL). The national governing bodies are the Council of Ministers and the following ministries: Ministry of environment and water (MEW), Ministry of regional development and public works (MRDPW), Ministry of agriculture and food (MAF); Ministry of economy and energy (MEE), Ministry of emergency situations (MES). The most important of them is the MEW. A special consulting authority was created to it and it is the National Council of Water designed to assist the ministry in running its water management policy with the aim of achieving equilibrium of public interest, protection of public health and sustainable economic development.

River basin level (RBL). There are four Basin Directorates, corresponding to the four specified basin management areas: Basin Directorate Pleven (Danubian area), Basin Directorate Varna (Black Sea area), Basin Directorate Plovdiv (East Aegean Sea area), Basin Directorate Blagoevgrad (West Aegean Sea area), each of them with a Council (Basin Council). They all are subjected to the MEW.

The structure of the institutions responsible for water management could be seen on Figure 1 below.

The water quality assessment and control that the institutions mentioned above perform use a number of standards for sampling and water quality analyses, such as BNS EN, BNS ISO, EN, ISO, validated methods according to the APHA-AWWA-WPCF Standard Methods for Examination of Water and Wastewater, etc. Application of so many different standards and methods has got only one essential goal, namely to take the best of Bulgarian and international achievements in that area and put them to use to real-life's work.

Very important for having good water management is not only to have good legislation, but also to find the best way for its implementation to real-life's work. An example of how theory (legislation) is put into practice, in this article, was taken from the domain of wastewater treatment.

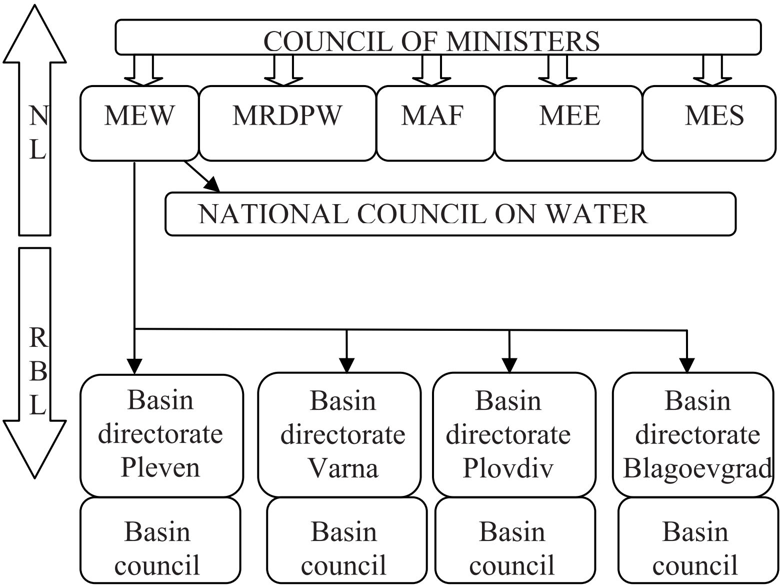

Figure 1. Scheme of the institutions.

The Wastewater Treatment Plant (WWTP) of Sofia city was taken as an object of examination for the year of 2002. The WWTP of Sofia is the largest in the country. It has been designed to have two mirror stages each with capacity of 500,000 m^3/day inflow, but only one of them has been built. The designed inflow data, based on several years of research, have been:

- Biological Oxygen Demand for 5 days (BOD_5) = 220 mg O_2/dm^3
- Suspended Solids (SS) = 316 mg/dm^3

Nowadays these levels were not appropriate and after a rehabilitation of the plant they were reduced to:

- Biological Oxygen Demand for 5 days (BOD_5) = 180 mg O_2/dm^3
- Suspended Solids (SS) = 160 mg/dm^3

The necessity of this lowering was due to the fact that after 1990 the country's economy collapsed and a lot of factories, plants and companies stopped operating and were closed. That led to a drastic decrease of the wastewater inflow in the WWTP and of the quantity of the pollutants in it.

- Water inflow: **1990** – 500,000 m^3
  1995 – 400,000 m^3
- Pollution of the inflow: **1989** – BOD_5 – 320 mg O_2/dm^3
  SS – 160 mg/dm^3
  1995 – BOD_5 – 160 mg O_2/dm^3
  SS – 100 mg/dm^3

After that every new factory built, opened or rehabilitated was modern and obliged to have its wastewater treated in its own local wastewater treatment plant, if needed before discharging it into the city's public sewage system.

The assessment and control of untreated and treated wastewater is being performed regularly on several places in the plant, having the following parameters analyzed: flow discharge, temperature, pH value, SS, chemical oxygen demand (COD), BOD_5, dissolved oxygen (DO), total nitrogen, organic nitrogen, ammonium ions, nitrite ions, nitrate ions, total phosphorus, organic phosphorus, heavy metals' ions and the following microbiological parameters: fecal coli forms, microbial number, ammonium producing micro-organisms, staphylococci, choleric vibrio. The basic parameters, monitored and controlled are, BOD_5, COD and SS. Different forms of nitrogen (N) and phosphorus (P) in water are still only defined, as stated above, since there is a gratis period till 01.01.2011 during which the country should equip the existing wastewater

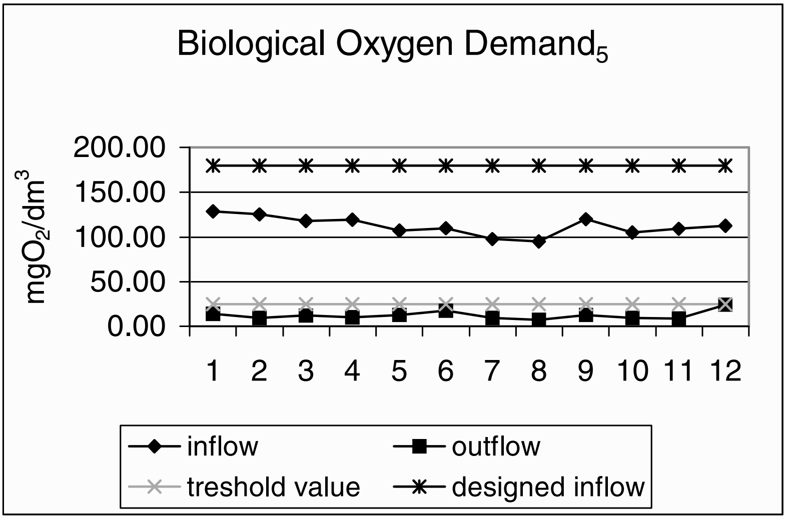

Figure 2. BOD$_5$ variations in the WWTP for 2002.*

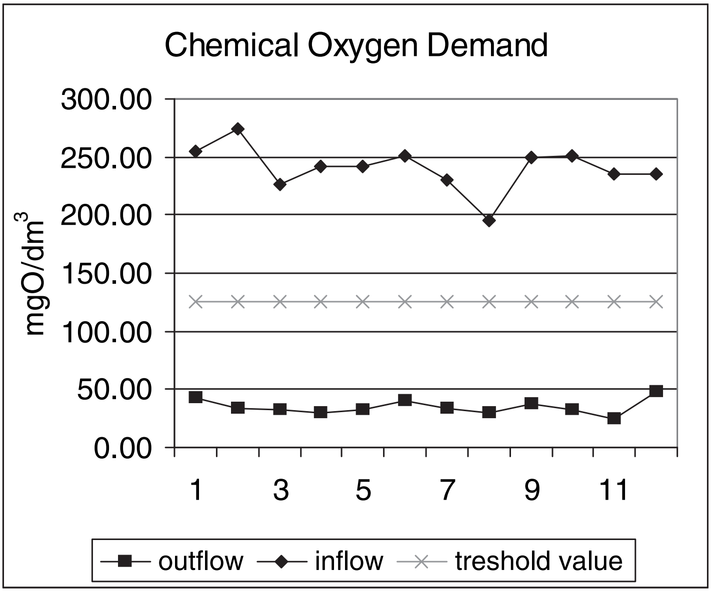

Figure 3. COD variation in the WWTP for 2002.*

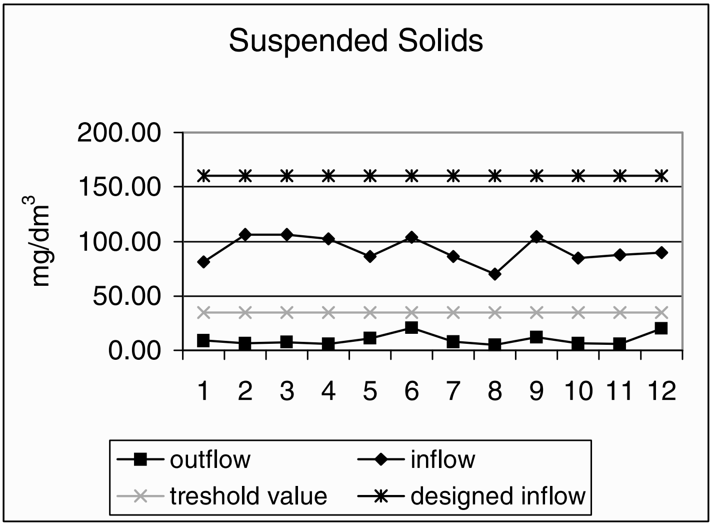

Figure 4. SS variation in the WWTP for 2002.*

* data source for the graphics – WWTP Sofia city

treatment plants and prepare them to remove the different forms of nitrogen and phosphorus from the wastewater that is being treated. The assessment of BOD_5, COD and SS variations of untreated and treated wastewater in the WWTP of Sofia city shows that the plant is not overloaded and the parameters' values in the outflow at the end-of-the-pipe meet the requirements given in Regulation No. 6 from 09.11.2000 that corresponds to Directive 91/271/EEC from 21.05.1991 and deals with the work of wastewater treatment plants.

The variation of BOD_5, COD, and SS values in the inflow and outflow of WWTP for 2002 is shown on Figures 2, 3 and 4.

The outflow should meet the requirements of Regulation No. 7 from May 1986 at the point of discharge in the running surface water, as well. Regulation No. 7 is about the quality of running surface water. There are three categories of running surface water according to it:

I category: $BOD_5 < 5$ mg/l O_2
COD < 25 mg/l O
SS < 30 mg/l

II category: $BOD_5 < 15$ mg/l O_2
COD < 70 mg/l O
SS < 50 mg/l

III category: $BOD_5 < 25$ mg/l O_2
$COD < 100$ mg/l O
$SS < 100$ mg/l

Regulation No. 6 allows the maximum values of BOD_5, COD and SS to be:

$BOD_5 < 25$ mg/l O_2
$COD < 125$ mg/l O
$SS < 35$ mg/l

As it could be seen the maximum values for SS given in Regulation No. 6 fit in both second and third category, the BOD_5 values fit only in third category, but the COD values do not fit in any. In case the value of COD of the treated wastewater is between 100 and 125 mg O/l, nevertheless that it fulfils the requirements of Regulation No. 6 such water cannot be discharged in any running surface water body because it creates a risk. Furthermore most of the running surface water bodies, which accept discharge of treated wastewater, are II category. Although it is considered that the purified wastewater continues to self-purify in the discharge channel it is very seldom possible to achieve the desired purification that way. The channel is just not long enough in most of the cases. Such kind of conflict appears because of the fact that the requirements of Bulgarian Regulations in use are stricter than those of the European Union, which came in force in Bulgaria. That reveals a need of respective modifications of the legislation within due limits.

3. Conclusion

The water and wastewater assessment and control in Bulgaria are being performed according to the Bulgarian Laws, Regulations and Standards that correspond to those of the European Union but some modifications of the Bulgarian legislation are still needed. The water and wastewater assessment and control is good tool, not only for environment and human being protection, but also for technological means of evaluation, or improvement of the environment and water, in particular. They are very essential when risk assessment is made, because they are basic for defining the level of the risk. The more precise they are, the more accurate the risk assessment is. Protection of the environment is one very complex process. It depends on many different aspects. The characterizing of impacts on water resource that valuates its quality is very important and that is why the water quality assessment and control are essential.

Starting out from Directive 2000/60/EC of the European Parliament and the Council of European Union, reviewing different institutions, at the end it’s time to pay attention to the consciousness and environmental concern of the common people. Although it seems impossible for a common person to do anything about improving or protecting the water quality it is simple reality that pollution of water is mainly almost 100% caused artificially. People in Bulgaria should start being more concern about the environment and realize that the small details of the ecological problems depend on them. A simple example is the dispose of used batteries or the separation of the household waste. Every single kind of waste that enters a dung-hill is a potential source of toxic contaminants. The more waste products get recycled, the more resources are spared and the less pollution there is.

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Regulation No. 6/2000 on emission standards for maximum admissible limits for dangerous and hazardous substances in wastewater discharged into water bodies, State Gazette 97/2000

Regulation No. 7/1986 about the parameters and norms for defining the quality of the running surface water, State Gazette 96/1986 http://ga.water.usgs.gov/edu/earthhowmuch.html http://www.learner.org/channel/courses/envsci/unit/text.php?unit=8&secNum=6

RISK ASSESSMENT OF OIL MARINE POLLUTION

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Abstract. Pollution of the marine environment by oil spill is a critical problem with worldwide ecological consequences. Assessing the risk of oil spills from ships has long been of interest to the maritime industry. Many factors affect the frequency of accidental oil spills, including the amount of oil transported and the combined effect of local condition, like weather and sea conditions, visibility, water depth, navigational hazards and nature of the sea bed. Oil is frequently stored and transported on the chemical tankers or product carriers. In case of accidental oil marine pollution there are a series of actions which must be taken.

Keywords: black Sea, oil marine pollution, aqua-barrages, dispersants, risk assessment

1. Introduction

The Black Sea is one of the most remarkable seas in the world. Below 250 m the dissolved oxygen is absent and the organic matter degradation uses oxygen bound in nitrates, and especially in sulfates, which generates hydrogen sulfide. Hydrogen sulfide has contaminated 90% of the water volume of the Black Sea, allowing the existence of only anaerobic bacteria (Titov, 2007).

Danube, Dnieper and Don are the largest effluents of Black Sea and they bring large amounts of pollution into the ill-flushed sea, including nutrients, raw sewage, oil and heavy metals from industry (Zaitsev, 1998). The tankers which transport chemical substances or oil are important sources of pollution even if acting by an indirect way.

The main sources of marine pollution are (Fabry et al., 1993):

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- Land-based sources and activities
- Dumping
- Seabed activities, both near and offshore
- Atmospheric sources
- Shipping and other sea-based activities such as fishing and aquaculture

2. Oil Marine Pollution

Marine pollution is defined by the Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), which is part of the basic framework of the United Nations Convention on the Law of the Sea (UNCLOS), 1982 is the:

> *introduction of man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water, and reduction of amenities.* (United Nations Convention on the Law of the Sea, 1982)

Marine chemical pollution is represented by the ingress into sea water of organic or toxic chemical substances which can act as pollution facts for a short or a long period of time. The most encounter consequence produced by the chemical pollution of the water consist in influence of the various polluting substances on the biological process, which rule the cycle of life in the marine environmental is the ecological effect.

Oil pollution is the most important danger to the marine ecosystem. Oil and oil product spillages at sea take place all the time (Ciuciu et al., 2006). Oil is a general expression to designate a viscous liquid having a density less than that of water. It can include 284 crude oils varying in proportion, and refined oils (such as diesel oil, heavy fuel oil, lubricating oil, kerosene and gasoline). Some oils are toxic to marine life; others are harmful partly due to their smothering effect when deposited.

Three main groups of oil can be distinguished in accordance with their appearance when floating on the sea surface:

- Light refined products (petrol, gasoline, kerosene) which spread uniformly on big surfaces and undergo strong evaporation and rapid natural dispersion processes, often resulting in their total disappearance in 2 to 3 days. They form thin sheens.
- Heavy refined products (types of fuel oils used by merchant ships) which are very viscous spread less rapidly and do not disappear naturally. These

form dark thicker patches, separated by areas of intermediate and thin sheens and may form emulsions with seawater.

- Crude oils whose characteristics and behavior vary greatly according to their type and origin. Usually these rapidly break into areas of dark, thicker oil interspersed with areas of intermediate and thin sheens. Most crude oils will form emulsions within 24–48 h (Manual on Oil Pollution at Sea: Securing Evidence on Discharge from Ship, Bonn Agreement, 1993).

Complex processes of oil transformation in the marine environment start developing from the first seconds of oil's contact with seawater. The main characteristics of oil transformations are their dynamism, especially at the first stages, and the close interaction of physical, chemical, and biological mechanisms of dispersion and degradation of oil components up to their complete disappearance as original substances (Readman et al., 2002).

The principal sources of oil spills for marine pollution are:

(a) The Danube river: About 110,000 t of oil is introduced into the Black Sea each year, and about 50% comes from the Danube. The rest comes from land-based sources, due to inadequate waste treatment and poor handling of oil and oil products.
(b) Offshore production discharges: In the Black Sea, the leading role in oil input belongs to land-based sources, which are dominated by river inflow.
(c) Shipping activities: This is one of the most important sources of operational oil pollution. Oil transportation and shipping activities are referring to the operational discharges from oil tankers, bunkering or oil transfer. Also there is an accidental oil pollution caused by tankers accidents (collision, grounding, hull failures, fire and explosion).

Large spills mostly resulting from collisions, groundings, structural damage like hull failure form serious threat for marine environment. However, occurrence of large scale oil pollution from shipping activities has declined over the years. Such events could have a disastrous impact on sensitive marine and coastal areas and is important to limit oil pollution by reducing the concentration of the more toxic polycyclic aromatic hydrocarbon fraction (Stanislav Patin, 1999).

3. Detection of Oil Marine Pollution

Detection of oil pollution is among the most important goals of monitoring of a coastal zone.

Oil pollution monitoring in the Black Seas is normally carried out by aircrafts or ships. This is expensive and is constrained by the limited availability of these resources. Satellite imagery can help greatly identifying probable spills over very large areas and then guiding aerial surveys for precise observation of specific locations.

Global Monitoring for Environment and Security (EMSA) provides a European operational system for oil slick detection based on satellite sourced synthetic aperture radar (SAR) images. The Synthetic Aperture Radar (SAR) instrument, which can collect data independently of weather and light conditions, is an excellent tool to monitor and detect oil on water surfaces. This instrument offers the most effective means of monitoring oil pollution: oil slicks appear as dark patches on SAR images because of the damping effect of the oil on the backscattered signals from the radar instrument. Nevertheless, detection based only on SAR data is still problematic because of the difficulty in distinguishing oil slicks, especially at lower wind speeds, from other phenomena known as oil "look-alikes" (Mityagina et al., 2007).

The service became operational in Romania in April 2007 and is under continuous development. Once the Member States have received information on potential polluters, they send out aircraft or vessels, when appropriate, to verify the existence of pollution and provide an appropriate follow-up, including the tracking of the polluter. EMSA should then be informed of the results.

4. Measures for Accidental Oil Pollution

Oil spill response methods are generally divided into three main categories:

(a) Mechanical recovery, where oil is contained in an area using boom or natural containment and removed using skimmers and pumps. Mechanical recovery contains the spilled oil using booms, and collects it with a skimming device for storage and disposal. Booms are deployed from vessels or anchored to fixed structures or land. A number of different kinds of skimmers exist; they use suction, oleophilic materials or weirs to remove oil from the water's surface. Once the oil has been recovered, it must be transferred using pumps and hoses to temporary storage until it can be properly disposed of. Therefore, an effective mechanical recovery system requires that sufficient equipment and trained personnel are available and conditions are conducive to contain, recover, pump, transfer and store oil and oily wastes. Ultimately, all recovered wastes must be properly disposed of according to applicable regulations.

(b) Manual recovery, where oil is removed using simple hand tools and techniques such as pails, shovels or nets.

(c) Chemical recovery using the following possibilities: In-situ burning or bio-remediation; Chemical countermeasures.

In-situ burning of spilled oil on the water's surface involves a controlled burn of floating oil that is contained to the appropriate thickness. The oil is ignited by releasing a burning, gelled fuel from a helicopter onto the oil, or by releasing an ignition device from a vessel or other access point. If successfully ignited, some or all of the oil will burn off the surface of the water. There will always be some residual non-volatile compounds that remain. This residue may float, sink or be neutrally buoyant depending upon the type of oil spilled and the conditions of the burn. Successful ignition and burning require adequate slick thickness for ignition, minimal wind and waves, and oil that has not emulsified (incorporated water) too much. If a burn is inefficient, a mixture of unburned oil, burn residue and soot will form. Downwind emissions must be below threshold levels for sensitive populations. Chemical herders, currently under development, may thicken a slick to allow for ignition.

The chemical countermeasures use a special group al chemical substances knowing as dispersants. According to literature data, there are two types of dispersants (Dragomir, 2004):

- The classic dispersants which are chemical substances based on hydrocarbon emulsifying and solvents.
- The concentrated dispersants, more active than the classics, are rapidly acting, producing a good dispersion of the hydrocarbons.

These substances are sprayed or applied to oil slicks to accelerate the dispersion of oil into the water column. The laboratory tests prove that the two types of dispersants can disperse a quantity of hydrocarbon equal of eight time more that their volume. They do not remove oil from the water, but are intended to limit the amount of oil forming a slick on the water surface or shoreline by driving that oil into a dissolved phase. Dispersants are applied from a vessel or aircraft using spray nozzles, pumps and hoses. Dispersant operations are usually monitored from aircraft to make sure that the application is effective and on target. Dispersants have a limited timeframe for effective application, requiring a prompt, accurate application of the chemicals to the spilled oil with the oil type, emulsification, salinity, weather conditions and sea state all aligned.

For better results a combination of two methods is recommended. First it is used the mechanical method which consist in launching of simple or double floating barrages which retain, localize and reduce the surface of the oil stain (Figure 1). After the oil stain is localized it can be used the second method which consist in dispersants applying using a vessel. The efficiency of this method depends on: the wind speed, oil stain dispersal into seawater, the oil emulsion, the aquaplane of oil thin coating.

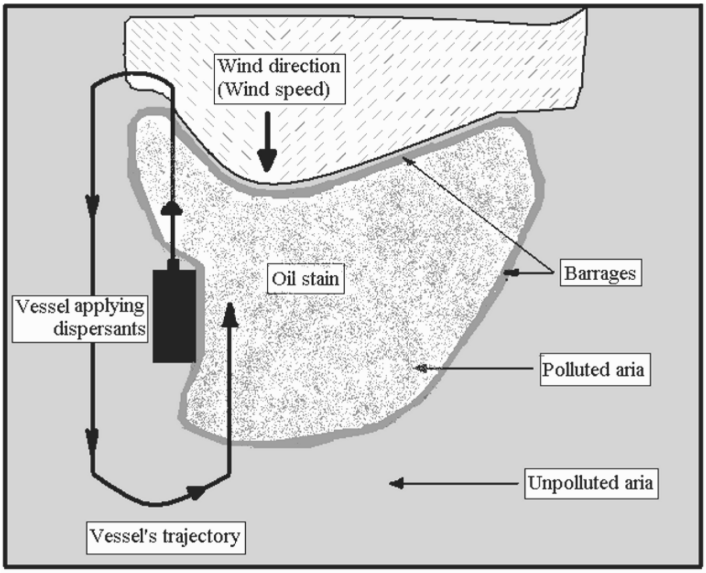

Figure 1. The neutralizing mechanism using barrages and dispersants.

All the measures require surveillance and spill tracking to identify the location, spreading and condition of the spilled oil in order to select and apply the appropriate response equipment and tactics. In the same time is required a logistical support to transport equipment and trained personnel to the spill site, deploy and operate the equipment, and decontaminate the equipment when response operations are complete. Spill responders must be able to safely access the spill site in order to deploy the equipment. All the measures can be taken as soon as is possible because oil is spilled to water, it begins to spread, evaporate and emulsify. As time passes, it generally becomes more difficult to track, contain and recover or treat spilled oil.

5. Risk Assessment of Oil Marine Spills

A formal risk assessment process offers several advantages to the management of oil spills. Firstly, it enables managers to identify the likely causes of oil spills for a specified area. Secondly, it enables managers to compare the relative risk between different geographical regions. Thirdly, it provides a basis for the identification of appropriate management strategies to reduce the overall risk for a given region, either through preventative or preparedness strategies.

Risk assessment is one step in the overall risk management process. Risk assessment underpins the preparation and planning for oil spill prevention and response strategies. The risk assessment is not attempting to quantify absolute risk, but determine relative risk between regions (Figure 2).

The approach to the risk analysis, in simple terms, involves:

- Hazard identification: What can go wrong and why
- Frequency analysis: How often can things go wrong
- Consequence analysis: How much harm can be caused by the event
- Risk calculation: Frequency or likelihood combined with consequence

A risk assessment has two components the "likelihood of an event occurring" and "the magnitude and of its consequences".

$$Risk = Consequence \times Probability$$

The consequence, or impact, of an oil spill is a function of a number of factors such as volume and type of cargo carried by a vessel at the time of an incident, effectiveness of the incident response and proximity to environmentally and economically sensitive areas. The probability of an oil spill relates to factors such as vessel traffic density, weather and sea conditions, navigational hazards, visibility, water depth and nature of the sea bed (Nautical Institute, 1999).

5.1. ANALYSIS

By comparing 2001 and 2007 tanker voyage data it was possible to illustrate the Black Sea areas in which there is the largest growth in total amount of oil transported and consequently growth in oil tanker traffic. Further, large increases are visible from the Port of Novorossiysk transiting through the Black Sea and the Bosporus Strait into the eastern Mediterranean and along the south east coast of Italy.

During the years 2001–2007 Russia has consistently increased oil production and has become the second largest producer of oil after Saudi Arabia. Volumes of oil and traffic transiting the Black Sea and through the Bosporus and Dardanelles have significantly increased; these areas are both environmentally and economically sensitive. The Bosporus, which at its narrowest point is only 0.5 miles wide, has suffered a number of large tanker spills in the past. Increased traffic in the region will contribute to an increased risk of oil spills.

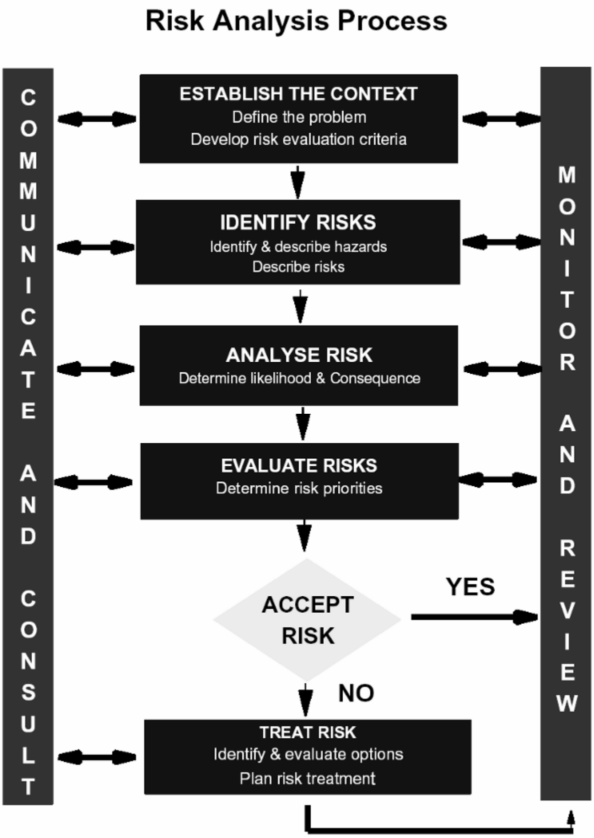

Figure 2. Risk assessment methodology flow chart.

Studies previously carried out by The International Tanker Owners Pollution Federation Limited (ITOPF) found that major spills (defined as greater than 1,000 t) are usually associated with serious casualties such as groundings, collisions, structural failures and fires and explosions and typically occur offshore or outside ports (Figure 3). Therefore many countries at risk are not large oil importers and the threat is therefore often related to traffic in transit to other regions.

The most serious accidents occurs on the Black Sea have taken place in the Turkish Straits, and in particular the Strait of Istanbul which connects the Black Sea to the Sea of Marmara. The Bosphorus, between the Black Sea and the Sea of Marmara is a very strongly driven international maritime route, is threatened by the heavy ship traffic, which exhibit an increased pattern of marine pollution. Today, the traffic volume exceeds 40.000 ships per year including

5.000 tankers, which corresponds to an average of 15 tankers per day. Oil pollution from accidents, ship activities and from the Black Sea at the Istanbul strait is about 80,000 t and increasing every year. (Polikarpov et al., 1994). Since 1960, over 40 heavy accidents occurred in Bosphorus. The two most serious accidents involved oil tankers.

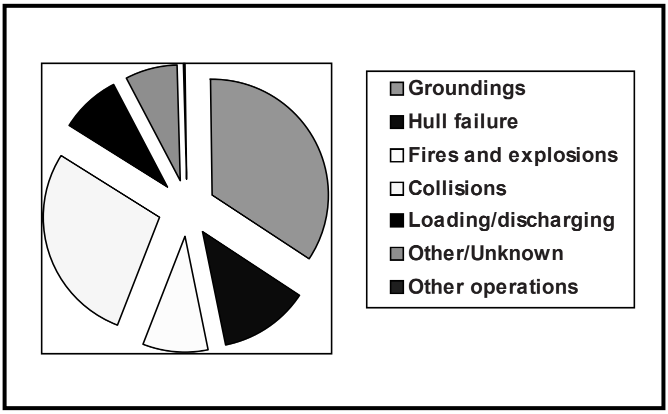

Figure 3. Incidence of spills >700 t by cause, 1974–2007 (ITOPF).

In 1979, a Greek freighter collided with Independenta, a Romanian tanker, causing one of the worst oil spills on record. After an enormous explosion, its crude oil load leaked into the sea. The crude oil polluted the sea surrounding the city, and kept burning for about a week causing heavy smoke. The Independenta accident has been ranked 11th in terms of the volume of oil spilled, yet in terms of physical impact and loss of life, it may take first place. Forty-three crewmembers tragically died in a fire that burned for weeks and 96,000 t of crude oil spilled into the sea and burned into the air. The Independenta was not the last time that an oil tanker burned and crewmembers died in a fire in the Turkish Straits.

In 1994, the Nassia, a tanker carrying 20,000 t of crude oil collided with the Shipbroker in the Strait of Istanbul near the entrance to the Black Sea. Similar to the Independenta, the Nassia collision resulted in a fire that killed 23 crew and spilled over 20,000 t of oil into the Strait.

6. Conclusions

Accidental oil spills, by their very nature, are unpredictable. A large oil spill does hurt people directly involved, the neighboring economies, the physical, chemical and the micro-biological parameters of state's territorial water. As tanker traffic will likely increase with the economical developments in the Black Sea countries, so will the probability of occurring a major accident that will affect all the countries in the Black Sea Region. The Black Sea countries should give greater attention to improving the quality of ships that are navigating the Black Sea because the increase risks of an oil spill and resulting pollution is very real. Oil is an essential fuel for the world. But so is the health of the environment vital for our survival. The loss of living marine resources in the Black Sea is a serious threat that cannot be underestimated.

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CASE STUDY ON GAS STATION ENVIROMENTAL QUALITATIVE RISK ASSESSMENT

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Abstract. An environmental qualitative risk assessment of gas station activity has been carried out. This paper describes the hazard scenarios considered, the qualitative risk assessment procedure and the discussions related to the calculated risks results. Taking into account the environmental risk that this particular activity presents due to the dangerous substances handling, we may consider this activity to present a moderate risk.

Keywords: hazard, accident, risk, risk assessment, environment, pollution

1. Introduction

Working activities will always involve hazard and accidental risks that can cause environmental damage and also can affect public health and employees' corporal integrity. As any industrial activity, a gas station activity represents a source of hazard, due to the use and handling of dangerous substances that are subject of regulation by national legislation, according to the Seveso II Directive.

There are several studies presented in the specialized literature, like the environmental level of aromatic hydrocarbons in a gasoline service station by gas chromatography (Periago et al., 1998) or the assessment of individual, social, and occupational risk for gas stations personnel (Santos-Mello and Cavalcante, 1992). Besides the risks related to the workers' security and health, gas station activities also present environmental risks that can be assessed through qualitative and quantitative analysis. Taking into account the possible risk scenarios that could take place, five tree-diagrams have been designed. For

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the identification of potential major accidents specific to the studied objective, a qualitative risk analysis associated to each scenario has been carried out. Risk has been calculated for each case scenario and integrated with probability and gravity in a matrix.

2. Legislative Framework

Major technological accidents are important mostly because of the impact on environment and public health. Industrial accidents involving dangerous substances are regulated at the European level through the Seveso Directives. Seveso I Directive (1982) excludes some activities, such as military emplacements, transportation of dangerous substances (railway, highway, air or maritime transport, pipes), loading and unloading activities inside docs. Therefore, more regulations have been adopted, as Seveso II Directive (1996) for the above mentioned supplementary activities, as well as Seveso III Directive (2003), to complete the regulations for other industrial activities, such as mining activities.

In Romania, the Seveso II Directive has been transposed through the following regulations (http://www.gov.ro/, http://www.mmediu.ro/):

- *Ministerial Ordinance no. 709/1999* (environmental audit elaboration and risk assessment)
- *Ministerial Ordinance no. 142/2004* (security report evaluation procedures for activities presenting major accidents hazard involving dangerous substances)
- *Ministerial Ordinance no. 647/2005* (methodology for emergency plans elaboration in case of accidents involving dangerous substances)
- *Ministerial Ordinance no. 1299/2005* (inspection procedure for objectives presenting major accidents hazard involving dangerous substances)
- *Governmental Decree no. 804/2007* (major accidents hazard control involving dangerous substances)

Risk can be differently defined, but in principle, risk represents the probability of occurring of a negative effect in a specific place and period and the qualitative evaluation of risk will consider the following factors:

- Hazard/source – pollutants identified or presumed to be existing on a emplacement, their toxicity level and particular effects.
- Action pathway – represents the path which the toxic substances reach the point where have harmful effects (soil, water, air).
- Target/receptor – represents the objectives upon the harmful effects of toxic substances action (human beings, animals, plants, water resources etc.).

According to the national legislation, the management of the Romanian companies presenting environmental risk should elaborate documentation regarding the environmental policies for accidents prevention. The policies establish the objectives and responsibilities for a safety operation of the company, taking into consideration the following aspects:

- Geographical position of the company – urban/rural areas, protected elements and emplacement's characteristics
- Substances – types and characteristics of substances presenting a potential hazard for the enterprise and environment
- Process – activities, installations, technological equipments presenting a potential hazard for the company and environment

3. Qualitative Methodology

Risk assessment is a basic component of environmental management system, and, together with risk management, represents a fundamental process that comes to solve the need of having a secure working environment that does not represent a threat to both humans and ecosystems. The main objective of the qualitative risk assessment analysis is represented by the identification of possible hazards.

The risk is evaluated according to the gravity levels and to the probability (Table 1), and risk calculation makes possible its classification and the qualitative analysis, as presented in Table 2 (Ozunu and Anghel, 2007).

The qualitative analysis of the risk takes into consideration both the gravity level (1–5) and the probability levels (1–5) of the accidents that might occur (Table 1). The gravity levels have the following significances:

- *Insignificant (1)* – no emissions; some unfavourable minor, short-term and reversible effects on parts of ecosystem and species.
- *Minor (2)* – emissions inside the objective emplacement; insignificant harm, rapid and reversible effects on parts of ecosystem and species: animals leave their natural habitat, plants are unable to develop, air quality creates a local discomfort, water pollution exceed the admissible concentration for a short period of time.
- *Moderate (3)* – emissions inside the objective emplacement retain with external help; temporary and reversible effects: migration of animals populations; plants are unable to survive; air quality is affected on a long-term by chemical compounds presenting a potential risk on health; possible effects on aquatic life; soil limited contaminations that can be rapidly remediate.
- *Major (4)* – emission outside the objective emplacement having no harmful effects; death of animals; broad habitats annihilation; air quality enforce to safety refuges or evacuation; soil remediation is possible by long-term remediation.

- *Catastrophic (5)* – toxic emissions outside the objective emplacement having harmful effects; death of animals; flora species annihilation; air quality enforce to evacuation; permanent and broad soil contamination.

TABLE 1. Risks matrix.

Probability			Gravity significance and levels				
			Insignificant	Minor	Moderate	Major	Catastrophic
Significance	Years	Level	1	2	3	4	5
Improbable	$<10^{-12}$	1	1	2	3	4	5
Less probable	10^{-8}-10^{-12}	2	2	4	6	8	10
Possible	10^{-6}-10^{-8}	3	3	6	9	12	15
Probable	10^{-4}-10^{-6}	4	4	8	12	16	20
Almost sure	$>10^{-4}$	5	5	10	15	20	25

The probability levels have the following significance:

- *Improbable (1)* – the event could occur in exceptional conditions; apparition frequency less than 10^{-12} years.
- *Less probable (2)* – the event might occur sometimes; apparition frequency between 10^{-8}–10^{-12} years.
- *Possible (3)* – the event can take place sometimes; apparition frequency between 10^{-6}–10^{-8} years.
- *Probable (4)* – the event could occur in many situations; apparition frequency between 10^{-4}–10^{-6} years.
- *Almost sure (5)* – the event could occur in most of the situations; apparition frequency higher than 10^{-4} years.

TABLE 2. Risk assessment.

Risk level intervals	Classification	Actions to be taken
1–4	Very low risk	Managing action through regular, routine procedures
5–9	Low risk	
10–14	Moderate risk	Managing action through specific standard procedures; work/ site managers implication
15–19	High risk	Prompt actions, very rapidly taken managerial decisions; high management implication
20–25	Extreme risk	Emergency situation, immediate actions, priority use of all available resources

From the gravity (G) and probability (P) levels given in Table 1, risk (R) is calculated by multiplying the two parameters and than filling the positions in the tabled matrix. The risk levels intervals, risk classification and the imposed actions are presented in Table 2. The higher the risk level value is, the greater priority for managing the risk is required. Considering the qualitative analysis results, any scenarios having a risk higher than 15, should further more detailed analysed (Ozunu and Anghel, 2007).

4. Case Study – Gas Station Associated Environmental Qualitative Risk Assessment

Our case study will present gas station activities having a potential environmental risk, and the associated qualitative risk analysis.

Gas stations are providing vehicle fuelling and other activities, such as cars' service, convenience shops. Several activities carried out in a gas station have the potential to release pollutants in the environment: fuelling vehicles, using the vehicle fuelling equipment, and storing fuels (oil and gas), therefore being risk sources. There are several pollutants to which human and environment are exposed: oxides (carbon dioxide, nitrogen oxides, sulphur dioxide), oil and gas.

The qualitative analysis follows the typical procedure:

- Risk identification, probability and gravity levels attribution
- Risk calculation and evaluation

We used the tree-diagram model (Robu, 2005), for the identification of existent risks on the emplacement of a gas station (Figures 1–5), representing the possible accidents scenarios grouped on the three main emplacements of the gas station: tanks, pumps, and atmosphere around the fuelling ramps. Based on the probability and consequences gravity attributed for each identified scenario, risk was calculated and a qualitative evaluation of the risk has been done.

4.1. ACCIDENTAL AQUATIC ECOSYSTEM POLLUTION AND FIRE RISKS AT OIL/GAS TANKS

The tree-diagram for this case scenario is presented in Figure 1.

For the evaluation of aquatic ecosystem pollution risk (scenario 1a) we considered that human errors generation is possible, due to the manual operation executed by the personnel during the tanks loading with oil/gas that might leak. Because the loading activity of tanks is not a continuous activity, taking place only when the tanks are refilled, the probability of risk regarding the existence of leakages at the oil/gas tank could be considerable. Furthermore, the subterranean surface where the tanks are emplaced is impermeable being covered with

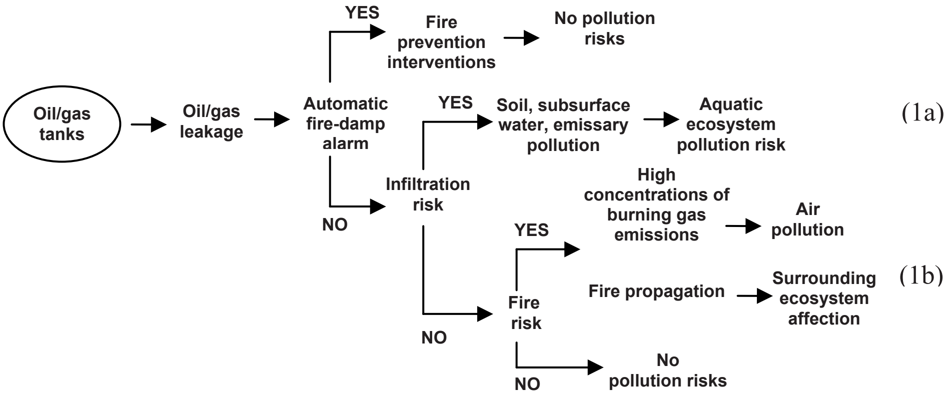

Figure 1. Tree-diagram for aquatic ecosystem pollution and fire risks at the oil/gas tanks.

concrete. Therefore, the existence of leakages at the oil/gas tanks is improbable (P = 1). The possibility of leakages at the oil/gas tanks lead to moderate consequences: contaminated soil but that can be rapidly remediate, plants unable to survive, pollution of subsurface water system (G = 3). The calculated risk value classifies the risk as a very low risk (R = 3). Trained operative personnel regarding the strict conformation to working instructions and tanks maintenance as well as periodical verification of tanks considerably reduce the risk of such accidents to occur.

For the accidental fire risk evaluation (scenario 1b) we considered that the ignition of the oil/gas inside the tanks might be favoured by high temperature having as consequence the evaporation of VOCs, but a fire source is necessary. In conclusion, a fire inside the tanks is improbable to take place (P = 1). Trained operative personnel regarding the strict conformation to operating and maintenance parameters and the existence of warning signals considerably reduce the probability of such events to occur. The possibility of fire in the oil/gas tanks could lead to considerable consequences to both human and environment: accidents of operative and/or intervention personnel, atmosphere emissions of burning gases, fire propagation (G = 4). The calculated risk value classifies the risk as a very low risk (R = 4). A preventive action that must be taken into consideration is the cooling installations that reduce the risk of similar accidents to occur.

4.2. ACCIDENTAL POLLUTION AT OIL/GAS PUMPS

Three tree-diagrams for accidental pollution at oil/gas pumps were designed: pollution of surface water with hydrocarbons (Figure 2), soil, subsoil pollution with oil/gas (Figure 3) and fire risks (Figure 4).

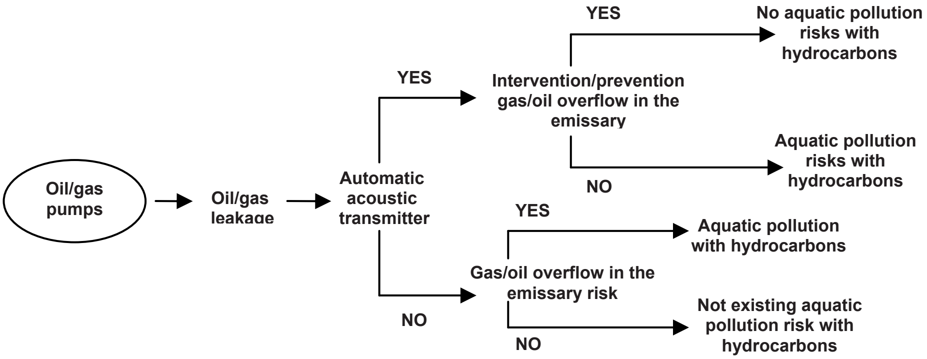

Figure 2. Tree-diagram for pollution of surface water with hydrocarbons at oil/gas pumps.

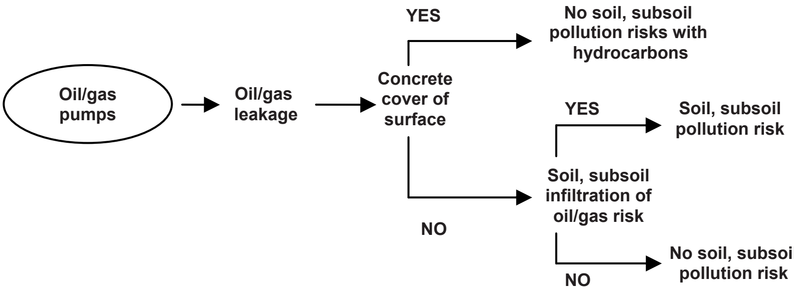

Figure 3. Tree-diagram for soil, subsoil pollution at oil/gas pumps.

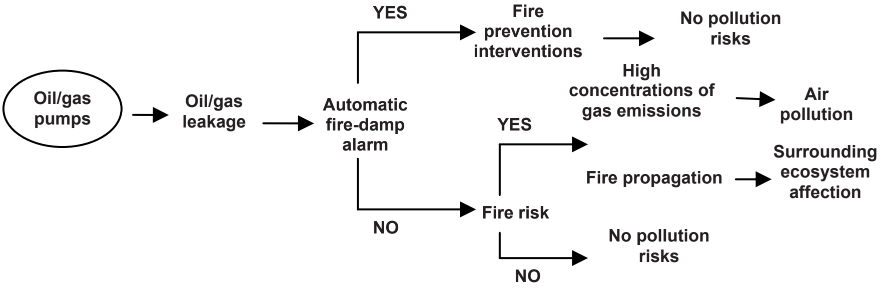

Figure 4. Tree-diagram for fire risks at oil/gas pumps.

For the evaluation of fire risk at oil/gas pumps we considered the risk possible to occur (P = 3) due to the higher atmosphere temperature, intense manipulation of oil/gas, existence of electrical installation of high capacity and existence of several potential leakage sources (used flanges, junctions). Fire at oil/gas pumps occur when the leakages are ignited. The consequences of similar events can be considered major (G = 4): atmosphere emissions exceed the admissible concentration, destruction of habitats, negative and long-term remediable effects on soil The calculated risk value classifies the risk as a moderate risk (R = 12). Strict conformation to operating parameters, periodical verification and maintenance of equipments reduce the risk of similar events.

4.3. AIR POLLUTION AT OIL/GAS FUELLING RAMPS

The tree-diagram for this case scenario is presented in Figure 5.

For the evaluation of accidental pollution of surface water system we considered the probability of leakage apparition at the oil/gas pumps higher than in previous case due to the intense manipulation of oil/gas, the higher pressure, the greater number of junctions where leakages could occur and the mechanically aged equipments use. Due to the much smaller quantity of oil/gas that might leak than in the oil/gas tanks scenario, the probability of polluting the surface water system is improbable to occur (P = 1) having minor consequences (G = 2): the concentration of pollutants in surface water system exceeds the admissible concentration but for a short period of time. The calculated risk value classifies the risk as a very low risk (R = 2). Similar, for the evaluation of accidental pollution of soil and subsoil due to pumps leakages, we considered the accident possible to occur (P = 3). The consequences are minor due to the small quantity of oil/gas that might leak (G = 2). The calculated risk value classifies the risk as a low risk (R = 6).

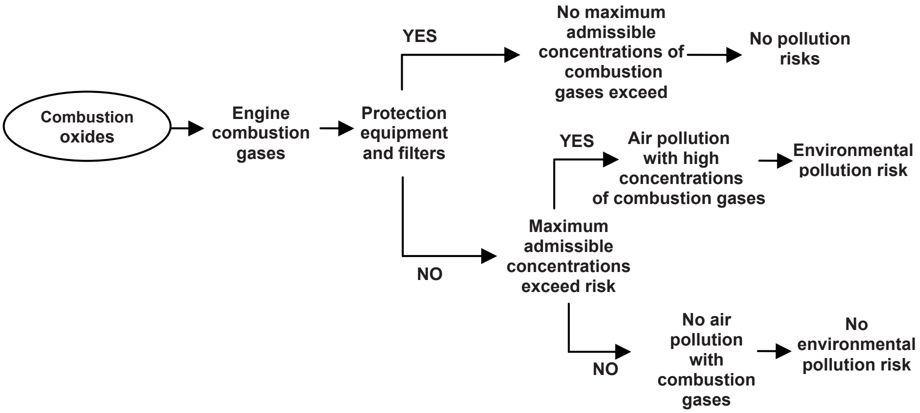

Figure 5. Tree-diagram for air pollution with combustion gases at oil/gas fuelling ramps.

Due to the increasing number of the cars refuelling, for this case, we considered the situation almost sure to occur (P = 5), presenting minor consequences (G = 2). The calculated risk value classifies the risk as a moderate one (R = 10). After-treatment exhaust gas devices, catalytic converters, particulate filters and improved fuel quality can reduce the concentration of combustion gases in the atmosphere.

4.4. RISK EVALUATION

The qualitative results from the risk assessment based on the five tree-diagrams, probability (P), gravity (G) and calculated risk (R), are presented in the probability–gravity matrix (Table 3).

It can be observed that whilst fire at oil/gas pumps is possible to occur having major consequences, a fire at the oil/gas tanks is improbable to occur; but, if this happens, will have major consequences on environment. Similar, oil/gas leakages at tanks is improbable to occur having moderate consequences on the environment, oil/gas leakages at pumps is possible to take place but having minor consequences on the soil and subsoil due to the quantity of oil/gas that exists in the emplacement.

The higher risk assessed (R = 12) was found in case of fire at the oil/gas pumps having, in the same time, major consequences on environmental media: air, water, soil. The scenario that presents the higher probability is in the case of air pollution with combustion gases (P = 5) due to the increased number of cars.

TABLE 3. Probability–gravity matrix.

Scenario	Hazard	P	G	R
1a	Leakages from oil/gas tanks	1	3	3
1b	Fire at oil/gas tanks	1	4	4
2	Water pollution by leakages from oil/gas pumps	1	2	2
3	Soil, subsoil pollution by leakages from oil/gas pumps	3	2	6
4	Fire at oil/gas pumps	3	4	12
5	Air pollution by combustion gases from fuelling ramps	5	2	10

5. Conclusions

Following the source-pathway-receptor, the designed tree-diagrams covered the worst case scenarios that might occur inside the gas station emplacement. Corresponding to each scenario, risk was calculated and presented, centralized, together with probability and gravity values, in a matrix, for a better illustration and understanding. Considering the risks values obtained, we may consider this activity to present a moderate risk.

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ENVIRONMENTAL RISKS ASSOCIATED TO THE USE OF CYANIDE TECHNOLOGY FOR GOLD EXTRACTION IN ROMANIA

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Abstract. The paper intends to approach some of the risks related to cyanide technology in gold mining, with particular focus on the closure phase. The Romanian mining industry is subjected to various environmental problems nowadays. Despite the significant efforts to support the thesis according to which "*All starts with mining*", it is more and more circulated that mining is incompatible to the sustainable development of the society. In a certain situation, only the modern – efficient and clean – technologies may provide to the mining industry a way towards survival and even towards development. Mining for closure is also very often met in the mining literature, as one has to take care of the sustainable use of a mining site after being closed.

Keywords: environmental risks, cyanide technologies, mine closure, sustainable development

1. Introduction

In the current phase, in the extraction activity and valorification of gold ores, one should place the accent on the application of clean technologies, from the beginning of the activity of a mine, up to its final or temporary closure. While most of the cyanide used by the industry is handled without obvious negative impact, the unique chemical behavior and toxic nature of these

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compounds, combined with the risk of serious mine waste spills, suggest that this topic deserves a closer look. Cyanide compounds are widely used by the mining industry to assist in the extraction of both precious and non-precious metals from rock. In gold mining, a dilute cyanide solution is sprayed on crushed ore that is placed in piles, commonly called heaps, or mixed with ore in enclosed vats. The cyanide attaches to minute particles of gold to form a water-soluble, gold-cyanide compound from which the gold can later be recovered. Consequently, cyanide and related compounds often are contained in discarded mine wastes.

Mining geochemical reactions may take many years to develop water-quality impacts. While gold cyanide-leach wastes are normally alkaline (pH 10–12), acid rock drainage problems can develop later.

Because gold-cyanide process fluids are kept alkaline, the potential to develop acid rock drainage may be overlooked. Spent ores or tailings that contain significant sulphide concentrations may become acid after the original buffering compounds and minerals react. These processes may require decades to become visible, and standard geochemical predictive techniques will often underestimate this potential. In the long-term, the acid rock drainage probably presents a much more costly contamination problem than do the cyanide and related products. Remediation of long-term acid rock drainage problems at mine sites usually requires the construction and operation of an active water-treatment plant.

Even after closure, the site is subjected to environmental damage due to the leach processes used in the past. Romania is confronted nowadays with the consequences of intense mining performed during the last decades when the production prevailed over the environmental protection. Nevertheless, the environmental damages have overcome the national borders, resulting in transboundary effects.

Unfortunately, the process of radical economic reform that Romanian mining is undergoing at the moment imposes financial impediments in rehabilitating the affected areas and in recovering these surfaces for future uses. One step forward would be taken by assuming the responsibility regarding past environmental damage and the binding of new enterprises to assume the current pollutant emissions, as well as to take the necessary protective measures.

The restructuring programmes in mining stipulate the closure of many mines in Romania, and in doing this, the environmental problems resulted from the use of chemicals, and of cyanide in particular, should be addressed properly. In this respect, good management and long term responsibility, based on coherent legislative framework are needed (Peck, 2005b).

2. Mining Industry in the North of Romania

The Maramures County, located at the Northern border of Romania with Ukraine, consists of the old “lands” of Maramures-Chioarul, Lapus and Baia Mare Depressions. The area is rich in gold, silver, lead, copper and salt and there is a long history of mining in the region. There are seven key mining sites in the county, which are potential point sources of pollution. The facilities produce gold (Au), silver (Ag), lead (Pb), zinc (Zn) and manganese (Mn). Waste waters and materials from these facilities are stored in flotation ponds and tailing dams, a standard international practice. However, the quality and protection available to such dams can vary depending on the location and the technology applied. For example, in Maramures County there are 19 flotation ponds identified by the local Environmental Protection Agency (EPA). Twelve of these are abandoned and seven are active sites. One of these is the Novat settling pond of the Mining Company Baia Borsa where a dam broke on 10 March, 2000.

Overall, the EPA lists 215 dams from mining operations on the territory of Maramures alone. Other sources of potential pollution include metallurgical plants. A site of a lead smelter at Baia Mare has been used for 150 years and is reported as being heavily contaminated. Air and water contamination are also reported. Other industrial plants in the area include a copper smelter and sulfuric acid plant. Decades of such industrial activity with insufficient waste treatment, only now being introduced, have resulted in a high level of chronic pollution of the ground, water and air of the region.

Therefore, mine operations continue to impact landscapes and leave behind massive environmental problems and liabilities, such as:

- Relief changes and displacement of households and of the industrial sites from the exploitation areas
- Occupation of large land surfaces for the exploitation, stockpiling, storage activity of the useful mineral substances, industrial facilities, etc., which thus become completely unusable for other purposes
- Land degradation by vertical and horizontal displacements of the surface and sliding of the waste heaps with the occurrence of serious accidents
- Pollution of flowing surface waters and of water table
- Negative influences upon the atmosphere, flora and fauna in the area
- Chemical soil pollution which might affect its fertile properties for many years, etc.

As a result of the transboundary effect of pollution, the environmental problems have exceeded the local character, as they are considered by humankind and the responsible factors at regional and even global level.

Romania, as part of a series of international conventions and agreements, has assumed the obligation and takes all the necessary efforts to comply with all the activity sectors and especially the industrial ones, within environmental protection international standards.

A special situation is that of the radical economic reform process that the Romanian mining is undergoing at present. The reform should provide not only the improvement of the economic performances, but also the mitigation of the environmental impact.

The demonopolization and privatization process may support these changes under the conditions when the responsibility regarding the past environmental damage is clearly defined and the coercitiveness of new companies to assume the current pollutants emissions and to take the necessary measures.

3. Cyanide Technology in Romania

The gold mines experienced many problems, such as cyanide spills, surface and groundwater contamination from acid mine drainage. This was one of the first massive cyanide heap-leach operations to open, as well as one of the first to close, leaving behind significant pollution and cleanup problems.

One of the major changes that contribute to deterioration in the risk situation, is that the cessation of industrial activities without planned closure measures (be it as a result of socio-economic turbulence, or for other reasons) is often associated with rapid deterioration in the condition of waste storage areas in the absence of maintenance activity and/or any form of monitoring. There are numerous abandoned or “temporarily abandoned” sites in the region that are gradually (or even rapidly) deteriorating with commensurate increase in risks to both local communities and international relations.

Baia Mare has a growing population and urban development with expansion restricted in some areas by the presence of old tailing ponds. In the early 1990s it was agreed that three such ponds should be cleaned and recovered to allow development to proceed. Residents are living within 50 m of highly toxic, potentially chronically leaking, waste sites that cause concern, especially in the dry months. There would be a clear environmental improvement from removing such waste sites.

Aurul was set up as a joint venture with Australian and Romanian partners following an international tender to clean up the sites. The design concept was that the waste would be transported away from the city (at least for two dams) where the remaining gold and silver in the tailings waste could be recovered using efficient modern technology that was not available when the original ponds were established.

It should be remembered that Aurul was not the only company extracting precious metals with cyanide. Next to the Aurul plant tailing dam there is the National Mining Company REMIN that operates a process similar to the one used by Aurul. According to the Baia Mare EPA authorities, the Remin dams were not built under proper conditions and do not have preventive measures installed such as waterproofing or installations of water spreading against the dust blowing, etc. As a consequence, the soil and groundwater in this area have been polluted before.

A WHO report "Concern for Europe's Tomorrow" identified Baia Mare as a "hot spot" and this area has a high level of potential and actual chronic contamination from a range of pollutants. The accident from January 2000 and any subsequent contamination that may have arisen from the Aurul plant needs to be seen in the broad context of long-term chronic pollution (UNEP/OCHA, 2000).

As per intention, the dam was therefore the most modern in the region, designed to be a major environmental improvement to the existing chronic polluting ponds. It was intended to be a safe and efficient method of meeting the requirements of the Romanian authorities and the Australian investors (Ulrich et al., 2005).

In conclusion, within the extraction of the gold ores and their valuable use, one should place the focus on the application of clean technologies and should reach an optimum combination of the environmental degradation prevention measures together with the application of adequate technological solutions (Georgescu et al., 2007). In this regard, the necessary actions should be performed to find new and efficient technologies for the environmental rehabilitation in the areas in need of immediate solutions and the introduction in parallel in mining of the most favorable technologies.

4. Risks Associated to the Use of Cyanide in Gold Extraction

4.1. RISKS ASSOCIATED TO CYANIDE BASED TECHNOLOGIES IN GOLD EXTRACTION

Cyanide is still used widely in the mining industry, either as a complexant reagent for gold and silver recovery, or as depressant reagent in the flotation circuits. According to the data provided by DuPont (USA), annually, in the mining industry there are used approximately 570 t sodium cyanide (the most frequently used type of cyanide).

Statistics show that the environmental major incidents caused by mining were not concentrated in a certain geographical area of the world (Moran, 2004). These incidents may take place probably in any geographical region, regardless of the size of the company, and it was noticed that they are not caused by a certain mining operation. Moreover, most of the major incidents occurred in the mining industry were the result of some accidental releases of refuse material from the tailings ponds, breaches, geotechnical deficiencies or natural calamities.

The most common sources of environmental contamination with cyanides are represented by: *The gases emitted from the coal degasification facilities*

- Installations for galvanic coatings
- Facilities for salts storage
- Mining industry:
  - *The tailing ponds in the mining industry* – which contain tailings and waste waters from the processing of ores or from the cyanidation of gold ores.
  - *The "heap leaching" technology of low gold content ores* – this gold recovery process implies the distribution of the sodium cyanide solution on a crushed ore heap, in order to lixiviate the material and dissolute the contained gold.
  - *The inadequate cyanide transportation, storage and handling practices, as well as the inappropriate cyanide packaging and long-distance transportation methods.*

Beside the presented contamination sources of the environment with cyanide, one should take into account also the *decontamination procedures applied*, which may lead to the formation of products or intermediate compounds extremely toxic for all the environmental factors (water, air, soil, terrestrial vegetation, aquatic flora and fauna, etc.). Among the most frequently used cyanide decontamination methods from the technological effluents we can enumerate: (a) oxidative: alkaline chlorination, hydrogen peroxide, Caro's acid, biodegradation, etc., and (b) non-oxidative: natural degradation, cyanide regeneration process, alkaline hydrolysis, flotation, etc. (Duffield et al., 1998). The compounds resulted as a result of these treatments may suffer changes under the influence of the atmospheric factors and of the microbiological processes (changes of pH, exposure to sun light, aerobe and anaerobic solubilization/leaching, etc.) causing the decomposing/degradation of metallic cyanides, of cyanates, thiocyanates and the forming of toxic compounds such as: *chlorine – cyan or cyanogen chloride* Cl–CN (favored by the pH decrease), *the* NC–CN *cyanogen* (favored by the pH decrease and the presence of the copper oxidized minerals), *nitrates, chloramines* and *ammonia*.

This "pollution source" is the more dangerous as there are no standards or norms (except the ammonia and nitrates) for the analysis of the technological effluents constituents, potentially toxic for the environment. None of the standardized analysis methods detects entirely the multitude of the cyanide compounds. Most of the environmental protection agencies or inspectorates impose the mining units the performance of analyses for the determination of total cyanides content and the maximum admissible concentrations for the waters discharged into the emissaries, not taking into account that these can still have potentially toxic levels (for fish, especially) of cyanates, thiocyanates or metal-cyanic complexes.

Of those mentioned above, there results that the type of the cyanides present as contaminants is very important in order to estimate the effects and risks upon the environmental factors. The multitude of different processes which interact in the natural systems (solubilization, decomposition, degradation, etc.) makes it difficult to predict the effects of cyanides upon the contaminated areas.

4.2. RISKS ASSOCIATED TO ALTERNATIVE TECHNOLOGIES

During the last years, there were investigated new processes for gold recovery from ores or mining concentrates, based on the use of some reagents considered less toxic than the cyanide.

Regardless of the technology used, the general risks are the following:

The major problems in the case of the mining exploitations and of the resulting wastes are as follows:

- The sediments from the tailing ponds contain heavy metals sulfates.
- the sulfates oxidize when they are exposed to air (oxygen) and water.
- Oxidation of sulfates causes a runoff loaded with metal acids.
- The runoff is generated for a long period of time.
- Usually the problems occur when there is a deficiency in acids absorption minerals (buffer).

In case of accidental failures and total collapse of the tailings ponds or of any type of mining wastes management systems may have short term effects but also possible long term effects.

The short term consequences include:

- Floods
- Sediment covering/suffocation of the affected vegetation
- Destruction and collapse of the affected infrastructure
- Obstruction of infrastructure
- Pollution of the affected environmental media (soil, vegetation, underground and surface waters)

Long term consequences include:

- Accumulation of metals in plants and animals
- Contamination of soil
- Loss of human life and animals

In the Table 1 there are analyzed the alternatives to replace the cyanide with other leaching reagents. For more than 100 years, the cyanide has been the most frequently used reagent in gold processing, but the environmental damages due to defective management required researches in the possibility of using some substitutive agents with lower environmental impact.

TABLE 1. Alternative technologies of the cyanide based gold extraction process.

"Alternative" reagent	Possible advantages	Disadvantages	Applications mentioned in literature
TIOUREEA	Technology confirmed, demonstrated Availability Recommended for refractory ores High speed of gold dissolution	Low recyclability due to decomposition Costs considered for the decontamination of the effluents Difficulties in controlling the process parameters Limited applicability	Wide scale application in: Australia, China, France (Miner Eng. 1999, vol. 12, No. 6)
THIOSULFATE	Confirmed technology Availability Recommended for refractory ores Performances in gold leaching (>99%)	Limited recyclability due to decomposition Costs considered for the decontamination of the effluents Difficulties in controlling the process parameters Limited applicability	Application at pilot scale in Nevada, USA (Hunter R. et al. Yes Technologies, Process Brochure)
THIOCYANATE	It may act in a wide pH range Partially recyclable	Limited availability Significant costs for the decontamination of effluents Needs higher temperatures (850°C)	Wide scale applications not known
BISULPHIDE	Availability Recommended for bio-oxidized pulps, in which bacteria may use sulphate ions and hydrogen for reforming the bisulphide ⇒ recyclable reagent	Dissolution speed extremely low (about 50% after 80 h) High costs for decontamination Limited availability	Wide scale applications not known

"Alternative" reagent	Possible advantages	Disadvantages	Applications mentioned in literature
AMMONIA	Availability Recyclable Recommended for refractory ores	Cannot be neutralized – it needs recycling Needs high temperatures and pressures for acceptable performances Uncertain selectivity	Wide scale applications not known
HALOGENS	Confirmed technology Availability Recommended for most types of ores Performances in gold leaching	Difficult process handling and control Needs an oxidant, most often halogen of the used halide	Use of the chlorine in refining gold is a verified technology Wide scale applications not known

By assessing these alternatives there resulted the conclusion that all are less efficient, more expensive, need extreme operation conditions (for example high temperatures and low pH values), need high concentrations and volumes of extraction agents and/or present risks for health or environment similar or sometimes higher than those presented by the cyanide. In addition, there is eliminated neither the construction of the tailings pond after processing, nor the associated risks.

All the gold extraction operations in the world nowadays use cyanide as filtering agent. It is a proved process, with well known risks and well established measures for the management, mitigation and reduction of risks. Until subsequent researches and developments are made, cyanide will continue to be the leaching reagent most frequently used in the gold extraction processes.

5. Mine Closure Strategy in Romania

As the costs related to ecological rehabilitation are significant and the available funds are limited, there are serious shortcomings regarding the protection of environmental factors and especially the reuse of the degraded lands and of the tailings heaps. The past focus placed on achieving high levels of production and the neglecting of the ecological impact have determined the accumulation in time of some serious environmental damages (Fodor and Baican, 2001).

In the restructuring programs of the mining industry there is provided the closure of some mines and exploitation sectors at national level, thus being created institutional structures for the management and implementation of programs in parallel with the completion of the legislative framework for the performance of these activities.

Many Romanian mines closed especially after 1990 due mainly to economic reasons. The state began to invest large amounts of money to support the mining industry. Although the subsidies were considerable, the exploitation losses continued to grow, rendering some mines not profitable any more. This led to a restructuring process of the mining industry, causing a lot of problems in the mining areas. The problems were mainly the economical decline, the enhancement of social issues and the aggravation of poverty (The strategy of the mining industry for the period 2004–2010, 2004).

Also, the closure was motivated by the low technological level due to the long use of the exploitation equipments, which could not operate under safe conditions. There remained many abandoned old structures, machinery, fuel tanks or buildings which became a threat to the safety of people and of the environment.

The financial losses of the mining companies and of the Romanian state have led to the decision of closing the mines which were not economically efficient. The restructuring strategy of the mining sector was developed for the purpose of the socio-economic regeneration of the mining areas. The Romanian Government and the World Bank finance the programme "Mine Closure, Environmental Rehabilitation and Socio-Economic Regeneration", which takes into account 386 localities in 22 counties.

In the year 2007, there were approved for closure 550 mines and quarries of which 168 are completed. As a result of this process of closing the non-viable mines, approximately 370 localities of 22 counties were affected from the social and economic point of view (Stefanescu et al., 2008).

In the closure and monitoring phase, a serious problem is raised by the large tailings disposal facilities. In Romania there are numerous tailings dams and waste heaps posing high environmental and health risks.

According to a report of the Romanian Ministry of Environment and Sustainable Development (MMDD) in 2007:

Twenty percent of the tailings dams are located in the valleys of some streams, inducing a high risk especially in the conservation and post-closure phases

- For most of the tailings dams, the storage of the flotation tailings is ceased.
- Ack of the surveillance and maintenance personnel for the tailings dams, during the post-closure monitoring.
- Structural instability of the hydrotechnical structures in some of the tailings dams may induce the increase of the accident risk.

– The design documentations and the regulatory papers for the operation, closure and ecological rehabilitation of the tailings dams are under various stages of performance.

As in all the stages of the mining activity, new technologies are also implemented in the closure phase. One good example is that of the gold heap leach facilities. In the 1980s the closure plans for these sites required the rising with fresh water in order to lower the pH and the cyanide. The worldwide experience regarding the closure of such sites has shown that the pH and the weakly dissociable cyanides are not the main subject of concern, but the heavy metals and salts (selenium, sulfate and nitrate) are.

As the closure plan of a mine should be outlined from the prefeasibility study stage, any change of the gold extraction technology during the exploitation period must be considered in order to be included and taken into consideration in the closure plan. The slightest change may cause various aspects regarding the closure and its associated costs.

6. Conclusions

A viable, sustainable mining industry is able to increase the economic level of a region, to diminish poverty in the respective region, and at the same time to help eliminating the economic differences in various regions and countries in the world.

The recent accidents in Romania have dramatically increased public awareness of the environmental and safety hazards of the mining industry. The Baia Mare accident showed that the level of public knowledge and understanding of risks inherent in mining and related industrial processes is very low. It also showed that there is insufficient communication between the various levels of authorities and the public concerning emergency preparedness, emergency response and damage prevention options and possibilities (Peck, 2005a).

The Maramures region, being an area of mining and related industries is of great economic significance to Romania and has the potential to create environmental problems downstream the Tisza River, which depends on the environment for its growing fishing and tourism industries and other economic activities. The importance of broader cross-border catchment area cooperation to the rehabilitation and further development of the region is apparent.

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EXPOSURE AND RISK ASSESSMENT OF ENVIRONMENTAL NITRIC OXIDES IN TUMOR PROGRESSION

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Abstract. Nitric monooxide (NO) and nitric oxides (NO_x) are the dangerous air pollutants possessing high nitrosative and genotoxic potential with adverse health effects. Environmental NO is related to nitrosative stress development in human body. Overproduction of NO has been implicated as a pathological factor in several forms of chronic human diseases, including cancer. The aim of this study was to evaluate exposure and risk associated with exogenic NO_x impact on the growth of model tumor Guerin's carcinoma (GC), xanthine oxidoreductase (XOR) activity, levels of mobile lipid domens (MLD), functional activity of peritoneal macrophages (PM) and lipid peroxidation (LPO) in tumor tissue. Exogenous NO_x inhalation leads to nitrosative stress development and toxic effect on cells of immune system *in vivo*. Tumor growth was accompanied by activation of PM. The prolonged inhalation of exogenous NO_x caused hyperactivation of PM (4.9-fold), increased MLD formation and total XOR activity (1.6-fold), and accompanied by accelerated tumor growth. In paralel observed sharp decrease (2.4-fold) of xanthine oxidase (XO) activity and LPO level (3.5-fold). The ratio of XOR isoforms increased by 18-fold mainly due to inactivation of xanthine dehydrogenase form (XDH). Reverse correlation was observed between the considerable increase of XOR activity in tumors and decline of GC nodes sizes. The high activity of enzyme in tumor tissues was accompanied by a 3.8-fold decrease in a final size of GC nodes as compared to tumors with lower activity of XOR.

Keywords: environmental nitric oxide, tumor growth kinetics, xanthine oxidoreductase, mobile lipid domens, lipid peroxidation, immune status

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1. Introduction

Environment pollution by carcinogens results in carcinogenesis and tumors promotion in many species of living organisms including human being. Nitric oxides (NO_x) are one of the major air pollutants possessing high nitrosative and genotoxic potential. Upon exogenous formation, mainly nitric monooxide (NO) is generated. In atmosphere it is oxidized to nitric dioxide which is toxic with adverse health effects. NO is a highly reactive and diffusible gas that is produced in a number of tissues, and exerts wide range of physiological and pathophysiological effects. NO participates in a variety of biological processes as a messenger, regulator and cytotoxic agent. Recent evidence indicates that most of the cytotoxicity attributed to NO is rather due to peroxynitrite, produced from the diffusion-controlled reaction between NO and another free radical, the superoxide anion. Free radical products of nitric monoxide and dioxide are able to damage proteins and unsaturated fatty acids, alter the activity of some enzymes, damage the integrity of cell membranes, inhibit electrons transfer in mitochondrial respiratory chain, decrease ATP level in blood and tissues of mammals, oxidize hemoglobin and take part in the generation of hemoglobin-NO conformers. These compounds possess mutagenic, carcinogenic and teratogenic activity (Lin et al., 2000; Pacher et al., 2007).

NO effect is related to the development of nitrosative stress in human body, namely in nitrosation of biological thiols, peptides, proteins resulting in alteration of their activity and in generation of carcinogenic nitrosocompounds *in vivo* (Espey et al., 2002). On the cellular level, the nitrosative stress caused by long-term NO inhalation or/and its endogenic synthesis may be linked to regulation of cell growth and apoptosis inhibition and as well in the pathogenesis of some human diseases including cancer (Tarr et al., 2006). The influence of exogenous NO on the development of tumor may be mediated by its action on the systems of antitumor resistance and is dose dependent. Certain concentrations of NO induce cell arrest, apoptosis, and even necrosis in susceptible cells, whereas other concentrations of NO can be antiapoptotic (Lancaster et al., 2006).

NO influences the level of free radicals in the organism. It easily reacts with other free radicals thus causing or their detoxication, or generation of extremely toxic forms (Kikugawa et al., 2004). The cytotoxic action of NO may be related to peroxynitrite (ONOOH) production (Felley-Bosco, 1998) – powerful nitrosative agent with higher reactivity then NO or superoxide radical (Muijsers et al., 1997). Peroxynitrite interacts with lipids, DNA, and proteins via direct oxidative reactions or via indirect, radical-mediated mechanisms. These reactions trigger cellular responses ranging from subtle modulations of cell signaling to overwhelming oxidative injury, committing cells to necrosis or apoptosis (Pacher et al., 2007).

Whilst endogenous NO is a factor of resistance against infectious agents, its effects are nonspecific. Hyperproduction of NO may cause damage of NO-producing tissues/cells (Thomas et al., 2002). In high concentrations NO inactivate enzymes, causes single-strand breaks of DNA and inhibits synthesis of DNA and protein (Kim et al., 1998; Nakano et al., 2003; Chien et al., 2004), plays important role in apoptosis (Kim et al., 2001). Neutrophiles and macrophages may generate NO upon inflammation. It was reported that excessive synthesis of NO by alveolar macrophages, epithelial and endothelial cells along with NO inhalation resulted in oxidative and nitrosative stress accompanied by the production of reactive intermediate forms of oxygen and nitrogen (Baran et al., 2004). An accumulation of NO may result in increased apoptosis of lymphocytes and macrophages and results in development of immune deficiency (Yook et al., 2004; Sarih et al., 1993).

The level of free radicals in the organism upon NO inhalation can also be largely affected by activity of xanthine oxidoreductase (XOR) isoforms. XOR is playing an important role in maintaining the balance of free radicals, takes part in NO circulation, in particular, it catalyze the reduction of nitrates to nitrites (Godber et al., 2001) and nitrites to NO (Godber et al., 2000; Li et al., 2001), organic nitrates – to inorganic nitrites, and organic nitrites – to NO (Doel et al., 2001). XOR is a complex molybdoflavoprotein identified as a terminal enzyme of purine catabolism, catalyzing the hydroxylation of hypoxanthine to xanthine and of xanthine to urate. The XOR protein is apparently expressed as xanthine dehydrogenase form (XDH; EC 1.1.1.204) but partially can be converted, either reversibly or irreversibly, to xanthine oxidase form (XO; 1.1.3.22) by post-translational modification (Hewinson et al., 2004; Harisson, 2002). The forms of XOR enzyme are differentiated by the preference of oxidizing substrate, either NAD+ or O_2, and generation of reactive oxygen species (ROS) – hydrogen peroxide and superoxide radical (Hewinson et al., 2004; Linder et al., 2003). At normal condition, XDH isoform predominates *in vivo*, producing potent antioxidant – uric acid (Frederiks and Vreeling-Sindelarova, 2002). Activation of XO isoform results in overproduction of the superoxide radicals in tissues and may cause intensification of lipid peroxidation (LPO) (Hosnuter et al., 2004; Sola et al., 2004). XOR possesses wide substrate specificity and takes part in metabolism of many xenobiotics and drugs. It is shown, that enzyme takes part in decomposition of S-nitrosothiols generated upon NO inhalation. In aerobic conditions, the S-nitrosothiols decomposition can be the source of reactive nitrogen species (RNS) – NO and peroxynitrite (Harisson, 2002; Trujillo et al., 1998). XOR itself can produce peroxynitrite, thus activation of the enzyme in the presence of NO may result in increased peroxynitrite synthesis (Godbeer et al., 2000). The majority of effects related to changes of XOR activity and conversion its forms associated with production of ROS and RNS. Activation of XOR and conversion of its XDH form to XO form leads to apoptosis and death of the damaged cells at pathological processes (Jackson et al., 1997). At the same time relation between enzyme activation, ROS and RNS production and subsequent damage of a genetic material which can cause tissues malignization was observed in a number of studies (Souici et al., 2000; Wright et al., 1999; Thom, 1992). Linder et al. detected feedback between poor prognosis of gastric and breast cancer and decreased XOR expression in tumors. They consider that XOR activity may be a new marker for a more aggressive gastric or breast cancer biology (Linder et al., 2005, 2006). The ability of the multifunctional enzyme XOR to perform general detoxification reactions and additionally, to synthesize large amounts of the antioxidant uric acid, or ROS and RNS, makes it a versatile intra- and extra-cellular protective housekeeping enzyme and an important component of the innate immune system (Vorbach et al., 2003).

^{1}H NMR-visible mobile lipid domains (MLD) are reported as a peculiar feature of malignant cells *in vitro* and *in vivo*, and cells undergoing apoptosis (Mountford et al., 1996). Cell membrane rearrangements coincident with malignancy and proliferation of tumor cells may contribute to the increase in the ratio of methylene (CH_2 at 1.3 ppm) to methyl (CH_3 at 0.9 ppm) resonance signal intensity as observed by proton nuclear magnetic resonance (^{1}H NMR). These resonances detected in many cancer cells and in cancer tissue. Cellular origin of these resonances is related to lipid turnover and cell membrane structure. NMR signals from CH_2 and CH_3 groups originate mainly from mobile fatty acyl chains of tissue triacylglycerides with lesser contributions from free fatty acids and cholesteryl esters. The presence of NMR-detectable lipids in cells can be originated from triacylglycerides in globular plasma membrane microdomains (22–28 nm in diameter) or intracellular lipid bodies, either adjacent to the plasma membrane or within the cytoplasm. Considering physical basis of NMR, lipid resonances must arise from the isotropically tumbling molecules, with sufficient molecular mobility (Hakumaki and Kauppinen, 2000; Quintero et al., 2007). All these findings make ^{1}H NMR spectroscopy as a very useful tool for noninvasive assessment of cell proliferation, malignancy and apoptosis. However, estimation of MLD level itself in many cases does not allow distinguish between proliferating or apoptotic cells.

The aim of this study was to evaluate exposure and risk associated with environmental NO_x impact on the development and growth of model tumor Guerin’s carcinoma (GC). A quantitative assessment of XOR activity, levels of mobile lipid domens (MLD), functional activity of peritoneal macrophages (PM) and lipid peroxidation (LPO) ware performed in tumor tissue.

2. Materials and Methods

Animal studies. Adult male rats (140–160 g) bred in the vivarium of R.E. Kavetsky Institute of Experimental Pathology, Oncology and Radiobiology, NAS of Ukraine (Kyiv, Ukraine) were used. All animals' procedures were carried out according to the rules of local Ethic Committee. Guerin's carcinoma (GC) obtained from the Bank of Cell Line of the R.E. Kavetsky Institute of Experimental Pathology, Oncology and Radiobiology (Kyiv, Ukraine). Male rats were divided into two groups: GC group – animals inoculated with suspension of GC cells and GC + NO group – animals were pretreated by inhalation of NOx for 1 month (16 h/day, average NOx concentration – 150 mg/m^3 of air) and then inoculated with GC cells. Suspension of GC cells (0.5 ml of physiologic solution containing 2.2 x 10^6 GC cells) was inoculated by intracutaneous injection in the rat thigh. Tumor growth was characterized by frequency of tumor appearance (% of tumor bearing animals per group), latent period of tumor growth and tumor volume (Y, in mm^3) at different terms of observation and calculated by equation: $Y = X_1 X_2 X_2 \pi : 6$, where X_1, X_2, X_3 are length, width and depth of tumor. On the day 18 after tumor transplantation, animals were sacrificed. The samples of tumor tissues were frozen in liquid nitrogen until analysis.

XOR assay. Total XOR activity and activity of XO were examined in post-mitochondrial fraction in fresh samples of tumor tissue (Battelli et al., 1992). Activity of XOR enzyme was estimated by the production of uric acid from xanthine (absorbance at 295 nm). Reaction kinetics were measured for 30 min at 26°C in special 96-well plates on the microplate reader Synergy™ HT (Bio-Tek Instruments, Winooski, VT, USA). In each well 250 µl of incubation mixture (50 mM sodium phosphate buffer with 0.3 mM EDTA, 0.5 mM xanthine, 0.5 mM NAD$^+$ and 0.24 mM oxonic acid) and $3.6 \cdot 10^5$ EAC cells in 50 µl of 50 mM sodium phosphate buffer with 0.3 mM EDTA were added. Oxonic acid was used as uricase inhibitor (Wright et al., 2004). Activity of XDH was calculated by the difference between XOR and XO activity, results were expressed in nM of uric acid per mg of total protein after 1 h incubation (nM/mg/h). Total protein concentration was determined according to Greenberg and Craddock (Greenberg and Craddock, 1982). Determination of macrophages cytochemical index of activity (CIA) was done by tetrazolium nitroblue test (NBT) (Savtsova et al., 2001).

LPO assay. Intensity of lipid peroxidation (LPO) was evaluated by spontaneous accumulation of malonic dialdehyde (MDA) and expressed in nM of MDA per g of tissue per h (nM/g/h). The absorbance of the colored thiobarbituric acid-reactive substances was measured at 532 nm on a Diode-matrix UV–Vis spectrophotometer Agilent 8453 (Agilent, Santa Clara, CA, USA) (Gatsko et al., 1989; Kessiova et al., 2006).

MLD assay. MLD level was estimated by ^{1}H NMR-spectroscopy. GC cells (10–12 $*10^6$) were washed with PBS, then twice with PBS made with D_2O to reduce protons signal from H_2O, suspended in a final volume of 0.6 ml of PBS-D_2O and transferred to a 5 mm NMR tube. ^{1}H NMR spectra were acquired using a 300 MHz Varian Mercury 300BB NMR spectrometer (Varian, Palo Alto, CA, USA) at 20°C. A glass capillary with 0.1% solution of TSP (sodium 3-trimethylsilyl (2,2,3,3-D_4) propionate) in D_2O was used as an external chemical shift reference at 0 ppm. The pulse sequence used to record cell pellet spectra combined presaturation of the residual water protons in the solvent and proton 1D experiment. Samples were spun at 20 Hz to prevent settling of cells during the experiment. Data were acquired over 5,000 Hz spectral width and digitized with 8k data points after accumulation of 128 scans. The signals at 0.9 and 1.3 ppm arising from $–CH_3$ and $(–CH_2–)_n$ groups of fatty acyl chains of lipid as well as signals at 3.2 ppm arising from choline-containing metabolites (Cho), which include choline and phosphocholine, were integrated using VNMR software (Varian, Palo Alto, CA, USA). A line broadening of 1 Hz was applied to the free induction decay prior to Fourier transform. GC cells spectra were characterized quantitatively by measuring the area of different peaks and expressed in relative units. The percentage of viable cells, determined by Trypan blue exclusion test, ranged between 90% and 95%, both before and after NMR analyses.

Statistical analysis. The results of the experimental and control groups were tested for statistical significance by a one-tailed Student's *t* test. Statistical comparison of peak area ratios and GC rate of proliferation or XOR activity was carried out using a two-tailed Student's *t* test. Significance level was set at $P \leq 0.05$.

3. Results and Discussion

In this study we evaluated risk associated with exposure to exogenic NO in tumor bearing animals. The kinetics of model tumor growth rate, corresponding activity of XOR, LPO and MLD formation in tumor cells have been analyzed. Mathematic model of "step growth" was used for an estimation of characteristic of GC growth and for the forecast of the final sizes of tumors. Special mathematical program was developed for approximation of data of tumors growth to the function of hyperbolic tangent. Criterion of the beginning of active GC growth was the size of tumors more then 0.25 cm^3. As the term of termination of the GC active growth period was selected time when size of the tumors was equal to the 90% of maximal predicted size.

The rate of effective transplantation of GC cells to experimental animals yielded 100% in untreated animals and 85% ± 10.0% in group of NO treated rats. The latent period of tumor development in intact rats (5.3 ± 0.2 days) or after NO treatment (5.9 ± 0.4 days) differs nonsignificantly ($p < 0.1$) and show only the tendency of NO influence on initial stages of tumor appearance and promotion of tumor growth beginning from day 12 after GC transplantation.

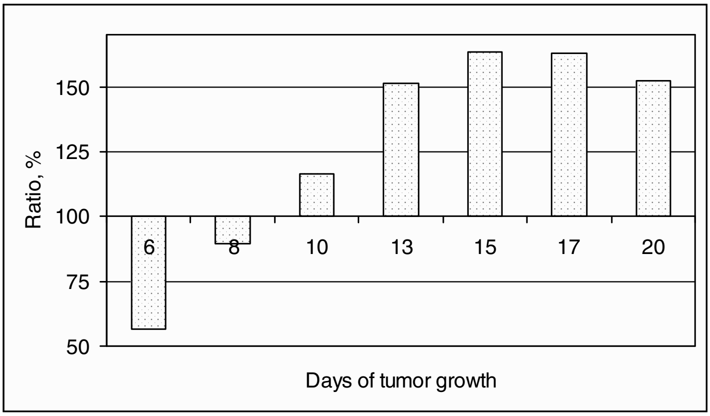

Figure 1. The rate of tumor growth in rats inhaled with NO expressed as a ratio of tumor volume in treated to untreated rats.

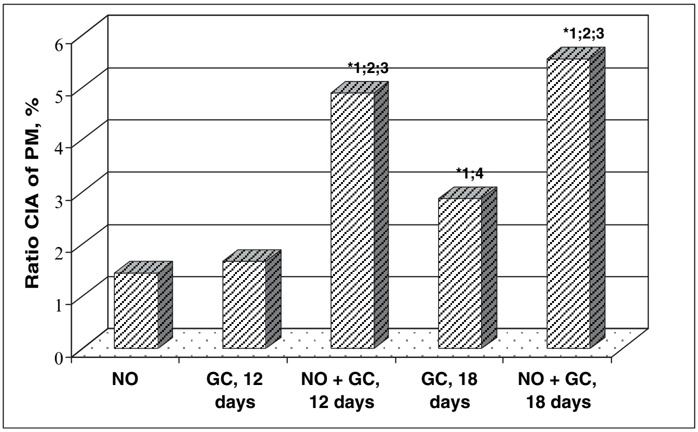

Figure 2. The effect of exogenous NO on functional activity of PM in rats expressed as a ratio of CIA in treated to untreated rats. $P < 0.05$ compared to control group ($*^1$); NO group ($*^2$); GC group ($*^3$); GC group, day 12 ($*^4$).

Dynamics of tumors growth of NO treated animals differed significantly from control group GC. Tumors growth was decreased at the first days after cells of GC inoculation (statistically significant differs up to 8 days of GC growth). Then tumor growth increased considerably, as compared to the GC group. Mathematical modeling allowed predicting prolongation of exponential phase of tumors growth in NOx + GC group for 7–8 days with 1.6-fold increase in the final size of tumor as compared to the GC group (Figure 1).

The effect of exogenous NO resulted in moderate increase of PM activity ($0.05 < p < 0.1$), but after GC transplantation its activity increased up to 72% as compared to untreated animals. At late term (18 days) of tumor progression activation of PM was statistically significant compared to control rats (Figure 2). These results suggest that GC transplantation and growth were accompanied by activation of nonspecific processes of antitumor immunity. Tumor development (12 days) in NO-pretreated rats was accompanied by marked increase of PM functional activity which was 4.9 fold higher than in untreated rats ($p < 0.001$) and threefold higher than in GC group ($p < 0.001$). At late term of GC growth in rats pretreated with NO, activity of PM was the highest among experimental groups pointing on their prolonged hyperactivation (Figure 2).

XOR activity in NOx + GC group was increased 1.2-fold in liver and 1.6-fold in lungs and tumor tissues. In tumor tissue the contribution of the XO form was 3.9-fold decreased and its activity was 2.4-fold lower as compared to GC

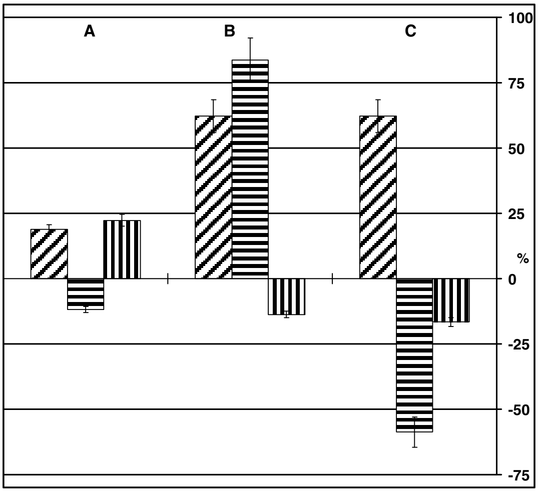

Figure 3. The total activity of XOR its XO form and level of LPO in liver (A), lungs (B) and tumor (C) tissues of rats treated with NO expressed as % to untreated group. ▨ – XOR; ▤ – XO; ▥ – LPO.

group. The contribution of XO form in total XOR activity in the liver and lungs did not differ significantly. It was decreased in liver and increased in lung ofanimals from NOx+GC group (Fig. 3). Basal level of XOR activity in tumor tissue of untreated rats was 220.36 ± 48.01 nM/mg/h at early term of GC growth with apparent domination (96.2%) of XDH isoform. At late term of GC growth, total XOR activity in GC cells raised 2.2 fold, but part of XDH was decreased (86.6%) due to post-translational modification to XO form. Exogenic NO treatment resulted in marked decrease of XOR activity compared to GC group (3.3 fold and 15.8 fold at days 12 and 20 respectively) along with alteration of the XO/XDH forms ratio. At the same time, the contribution of XDH isoform in total activity decreased from 43.8% to 26.8%.

There were no considerable differences of LPO level in organs of animals of group NOx + GC and GC. LPO was increased in liver (22%) and decreased in lungs (14%) of the rats pretreated with NOx. The level of LPO in tumors of rats pretreated with NO was significantly decreased at late term of GC growth and yielded 10.61 ± 1.44 nM/g/h versus 36.60 ± 3.20 nM/g/h in GC group (Figure 3).

The ability of the multifunctional enzyme XOR to take part in NO circulation, perform general detoxification reactions and to affect the balance of free radicals in cells makes it a versatile intra- and extra-cellular enzyme capable to mediate tumor development. An evaluation of the relationship between growth rate of Guerin’s carcinoma and XOR activity shown on Figure 4. Inverse correlation between XOR activity and the size of tumors at 18 days

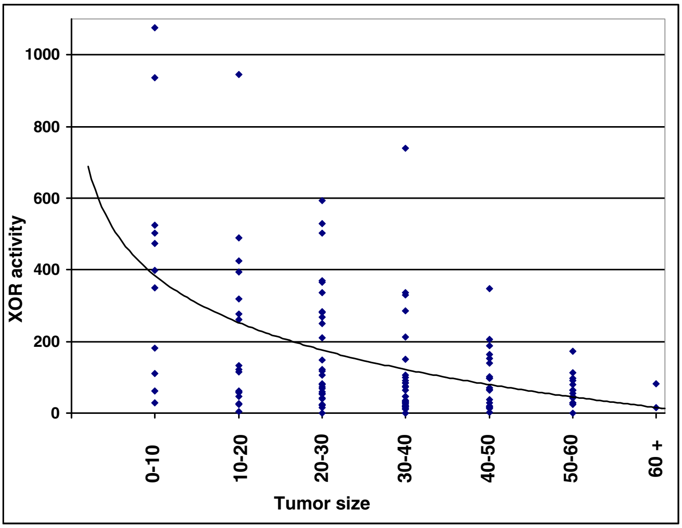

Figure 4. The XOR activity (nM/mg/h) in GC cells isolated from tumors with different growth rate (mm^3 ·10^3).

of GC growth was shown. The high activity of enzyme in tumor tissues (XOR activity in this group exceeded 500 nM/mg/h) was accompanied by a significant decrease in a final size of GC nodes (correlation coefficient $\rho = -0.89$; $P < 0.05$) as compared to tumors with lower activity of XOR. Changes in the size of tumors had more evident association with average activity of XOR (6.7-fold difference in opposite categories) then categorized XOR activity against the sizes of tumors (2.3-fold).

Cell membrane rearrangements coincident with malignancy, proliferation or apoptosis of tumor cells were assessed by ^{1}H NMR. The presence of NMR-detectable MLD in GC cells was studied in untreated rats and after pretreatment with exogenic NO (Figure 5).

The level of MLD, estimated by the ratio of methylene (CH_2 at 1.3 ppm) to methyl (CH_3 at 0.9 ppm) resonance signal intensity, was elevated in GC cells but did not increased during tumor progression. Inhalation with NO did not affect the MLD level at early term of tumor growth but at late term it was 1.4-fold increased. Cells isolated from tumor with diverse rate of growth yield different level of MLD formation. Direct correlation between MLD level and proliferation rate of tumor cells was revealed (Figure 6a). Highest MLD level agreed with high proliferation rate was registered in GC cells with lowest XOR activity. Increase of XOR activity (2-fold) at early term of GC growth coincides with 1.3-fold decrease of MLD level in GC cells. Further increase of XOR

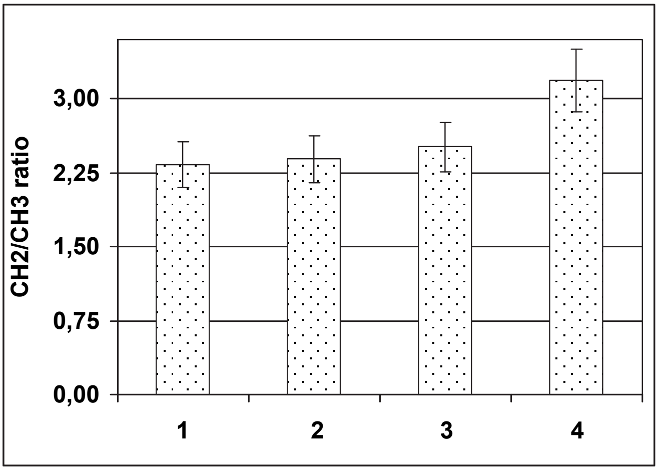

Figure 5. The MLD level in GC cells isolated from rats at different term of tumors development and pretreated with NO. 1 – GC, 12 days; 2 – GC+NO, 12 days; 3 – GC, 18 days; 4 – GC+NO, 18 days.

activity (7.5-fold) in tumor cells did not affect the mld level. However, at highest activity of xor and its xo form we observed upward tendency stipulated by free-radical production and apoptosis (Figure 6b).

4. Conclusions

The present study was intended to evaluate exposure and risk associated with action of exogenous NO on antitumor resistance of rats and the involvement of nonspecific processes of antitumor immunity, XOR, LPO activities and MLD formation in this process. Prolonged inhalation of NOx significantly changed the kinetic of GC growth in animals and this appears to be a two stages process (Figure 1). First stage begins after NO pretreatment as a result of nitrosative stress. Considering toxicity of NO metabolites, this may be reason for less effective GC transplantation and the increase of latent period of tumor

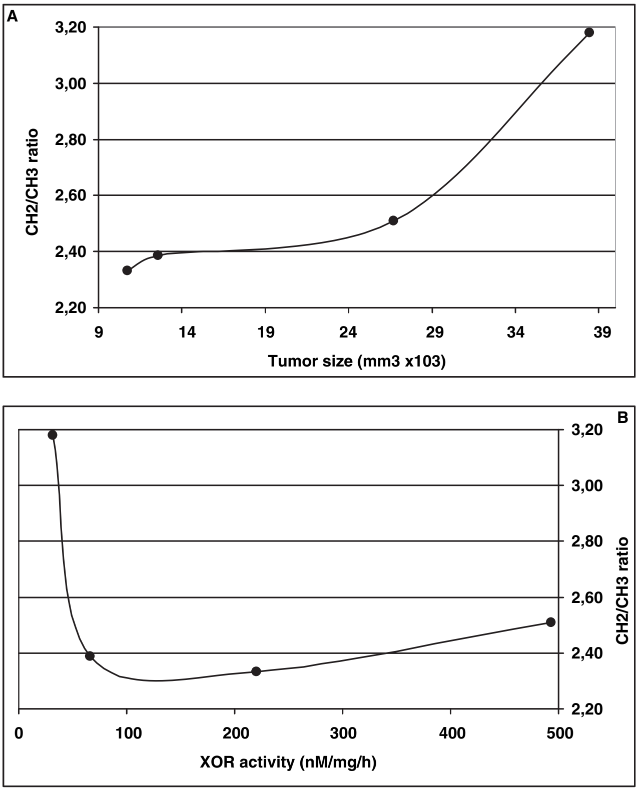

Figure 6. The MLD level in tumors with different growth rate (**a**) and different XOR activity (**b**).

development. In addition, elevated activity of XDH isoform was accompanied by generation of significant amount of uric acid (compound with known antioxidant properties [Frederiks and Vreeling-Sindelarova, 2002]) in tumor tissue, and existence of unfavorable conditions for production of superoxide and peroxynitrite as a result of hypoxia in tumor. Prolonged NO inhalation alone or early term of GC growth did not change significantly the activity of effectors of natural resistance, PM activity was only slightly increased reflecting a typical response of the organism on tumor cell transplantation (Savtsova et al., 2001). However, GC transplantation to NO pretreated animals resulted in hyper-activation of PM compared to intact rats. The detected increase of XO/XDH ratio in tumor tissue of NO treated rats was possibly caused by inactivation of the enzyme due to nitrosative stress.

Second stage of tumor progression was characterized by significantly promoted tumor growth and MLD formation in NO treated rats at late term after GC transplantation. The level of MLD in GC cells was increased in tumors with elevated proliferation rate but XOR activity was inversely correlated to the size of tumors and significant increase of XOR activity in tumors was accompanied by decline of GC nodes sizes. Increased presence of NO_x due to NO release by hyperactivated macrophages, along with S-nitrosothiol decomposition and marked decrease in XDH activity may result in the damage of tissues by free radical forms and decrease of immune resistance correlating with more intense tumor growth. Obtained results demonstrate that XOR activity, proportion of its forms in cells and MLD level estimated by ^{1}H NMR-spectroscopy may be used to monitor NO exposure and for risk assessment of environmental NOx and their impact on tumor progression.

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BLOOD-LEAD LEVELS IN SCHOOLCHILDREN FROM VELES, RELATED TO THE AMBIENT AIR POLLUTION BY LEAD

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Abstract. The objective of the study performed in 2001, 2003 and 2004 was to investigate and analyze the relationship between ambient air's pollution by lead and blood-lead levels in schoolchildren exposed to lead emissions in the city of Veles. The city of Veles, with its geographical position, atmospheric characteristics, urban and industrial concentration, and its improperly located the Lead and Zinc Smelter Plant upstream to the north wind opposite to the Wind Rose (north wind is dominant and dispersion of pollutants is going directly to the city), multiplied by inconvenient climate-meteorological, hydro-topographic factors has a huge and continuous air pollution problem. The Lead Smelter Plant, built in Veles in 1973, is located on the north of the city only 200–300 m away from first households. There was statistically high significant difference by Student t-test of the average annual concentration of lead in the ambient air in Veles in 2001 (x = 0.94 μg/m^3), compared to the 2003 (x = 0.22 μg/m^3) $t = 4.81$ $p < 0.0001$, and 2004 (x = 0.155 μg/m^3) $t = 5.53$ $p < 0.0001$. Registered average annual concentration of lead in the ambient air in 2001 was 89% higher than the recommended value from WHO and EU (0.5 μg/m^3). Increased concentration of lead in the ambient air, represent high risk factor for the health of the exposed children population in the city of Veles. There was a very high significant statistical difference between the blood-lead levels in the examined schoolchildren in 2001–2002 (n = 203 with average age x = 10.06), and schoolchildren in June 2003 (n = 31, x = 16.51 μg/dl, at the 12.8 age). The difference can be explained by stop of working of the Lead Smelter Plant (20 days without emission), and biological life-time of lead into blood and soft tissues. In 2004 as a fact on stopping of ambient air emission by lead the blood-lead levels in schoolchildren have significantly dropped (n = 93, x = 7.64 μg/dl).

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Keywords: blood-lead level, schoolchildren, lead, ambient air

1. Introduction

The aim of the study was to find out potential causal-relationship between ambient air lead's exposure and blood-lead levels in schoolchildren.

Placental transfer of lead occurs in humans as early as the 12th week of gestation and continues throughout development. Young children absorb 4–5 times as much lead as adults, and the biological half-life may be considerably longer in children than in adults. Lead is a general toxicant that accumulates in the skeleton. Infants, children up to 6 years of age and pregnant women are most susceptible to its adverse health effects. Renal tumors have been induced in experimental animals exposed to high concentrations of lead compounds in the diet, and IARC has classified lead and inorganic lead compounds in Group 2B – possible human carcinogen (WHO, 2004).

Lead is a cumulative common poison, cause of adverse health effects in vulnerable group of population – fetuses, infant and children up to 6 years, schoolchildren, pregnant women, and the others. Almost, all organs and systems can be potential targets, primarily for anemia and adverse effects to the central nervous system, kidneys, reproductive and immune system; as well cardiovascular, liver, endocrine and gastro-intestine effects. Under low level and long-term exposure as it is for urban population, most critical effects are those on blood and nervous system. In children lead causes adverse effects to nervous system by slowing the nervous conductivity, behavioral changes, as well weak slope of cognitive function, to mental retardation (blood-lead level 80 μg/dl), acute encephalopathy and death (blood-lead level 80–100 μg/dl). There is evidence that cognitive capability can be influenced under levels <15 μg/dl; but it cannot be assessed is it threshold for lead effects on neurophysiological development, and because of that exposure of young children shall be reduced to lowest possible level (WHO, 1987).

Lead appears naturally in earth crust with average concentration of 13 mg/kg and it is most present heavy metal. Lead contains mostly in galenite (lead sulfide). Lead in the environment exists almost completely, as inorganic lead (WHO, 1977). In the ambient air lead appears as a vapor and particles which are mostly in the street and industrial dust (Schilling, 1993). In natural, non-urban area lead level into the ambient air is lower than 0.5 μg/m^3, in urban area from 0.2–2.0 μg/m^3, and in vicinity of the Lead Smelter Plants from 1.0–2.0 μg/m^3 (WHO, 1989).

2. Material and Methods

In the frame of the study during 2001–2002 has been examined a group of school children from the City of Veles (n = 203, with average age x = 10.06).

In June 2003 have been examined representative sample of 31 children at the 12.8 age, from Veles-polluted area. In 2004 have been examined representative sample of 93 children at the 12.5 age, from the City of Veles.

Lead levels were analyzed in venous blood samples. 2 ml samples were obtained in sterile vacutainer, reconstituted with 1.5 mg K_2EDTA/ml blood, stored at +4°C and transported during the same day. Using AAS (atomic absorption spectrometer) with a Perkin Elmer 4100 HGA 700 graphite furnace fitted with an AS-70 brand Auto sampler. Lead was extracted into a mixture of nitric (HNO_3) and hydrochloric acid (HCl) under pressure with microwave digestion. A PAAR PHYSICA – PERKIN ELMER microwave furnace designed for laboratory practice was used. The research was approved by the ethics committee, as well by the parents of the examined children. The parents of the children have been informed about the results of the blood lead levels.

Lead in PM from the ambient air in municipality Veles (1 year monitoring/ every day measurement by High Volume Sampler), has been analyzed by AAS with graphite furnace, type PERKIN ELMER 4100, HGA 700 with Auto sampler AS-70. Software STATISTICA 7 was used for statistical operations in order to found significant difference, and correlations between two different groups of variables.

3. Aim

The aim of the study was to find out potential causal-relationship between lead's exposure and blood-lead levels in school children.

4. Results and Discussion

The city of Veles, with its geographical position, atmospheric characteristics, urban and industrial concentration, and its improperly located the Lead and Zinc Smelter Plant upstream to the north wind opposite to the Wind Rose (north wind is dominant and dispersion of pollutants is going directly to the city), multiplied by inconvenient climate-meteorological, hydro-topographic factors has a huge and continuous air pollution problem. The Lead Smelter Plant, built in Veles in 1973, is located on the north of the city only 200–300 m away from first households.

According to the approximation in 2001 in Veles have lived 67,178 citizens, 4,906 preschool children (0–6 years old), and 5,972 were schoolchildren (7–14 years old). Dominant wind direction according to wind rose is northwest wind (Statistical Annual, 2002).

There have been performed 1-year measurements of lead from the ambient air. During the monitoring, the Lead Smelter Plant has been working. The annual average lead level during 2001 has been 0.94 μg/m^3 and according to the WHO, is by 89% higher than the recommended value = 0.5 μg/m^3 (WHO, 2000). From the performed examinations of the ambient air's lead level in Veles, it was registered higher average annual concentrations of lead than the guideline value (0.5 μg/m^3). There was statistically high significant difference by Student t-test of the average annual concentration of lead in the ambient air in 2001 in Veles ($x = 0.94$ μg/m^3), related to the 2003 ($x = 0.22$ μg/m^3). In 2003 the average annual ambient air lead level was far bellow the recommended one (0.22 μg/m^3) (Table 1).

TABLE 1. Ambient air lead levels in particulate matters in Veles, μg/m^3.

Year of investigation	Average annual level	SD	Minimum	Maximum
2001	0.94	0.49	0.44	1.94
2003	0.22	0.18	0.06	0.73
2004	0.15	0.07	0.05	0.26
WHO recommended value = 0.5				

Student t-test $t = 4.82$ $p < 0.0001$ (2001 compared to 2003).

Student t-test $t = 5.53$ $p < 0.0001$ (2001 compared to 2004).

Student t-test $t = 1.16$ $p > 0.05$ (2003 compared to 2004).

In June 2003 the Lead Smelter Plant stopped to work. One year time distance without emission of lead in the ambient air has shown significant decrease of the average annual air concentrations of lead in 2004 (0.15 μg/m^3) compared to 2001. There was not found significant statistical difference between the average annual concentration of lead in the ambient air in 2003 in Veles ($x = 0.22$ μg/m^3), and in 2004 ($x = 0.15$ μg/m^3). From Table 1 can be concluded that there were registered lower minimum and maximum values of lead in the ambient air in 2003, as well in 2004. This contributes to the fact that there was registered improvement of the ambient air quality in Veles relating to the pollution by lead. Total emission level of lead in Veles is 85 folds above the MAC (maximum allowed concentrations), which means that daily is releasing 55.85 kg lead in the atmosphere, meanwhile total emission quantity of dust in the air is 10.6 folds higher than MAC, respectively in the city are discharging

2.6 t dust per day. The data relate to last 5 years, respectively from 1997 till 2002 (Balaburski, 2002).

Nriagu et al. (1996) have registered that in Africa, in urban and rural areas, and close to the mining centers, the average annual ambient lead level was 0.5–3.0 μg/m^3, and >1,000 μg/g in the dust and soil. Bainova (1996) has studied in 1991, 1992 and first 6 months of 1993 and she recorded that daily average lead levels in the ambient air, have been overpassed MAC of 1 μg/m^3 by 1.5–2.5 folds in the City Kardjali in Bulgaria. After that, lead levels in the ambient air have been decreased under the standard of the European Union. Normalizing of the ambient air quality has been resulted by overtaken measures from the Board of the Lead and Zink Smelter Plant in Kardjali for reduction of the emission of heavy metals.

In the frame of the study during 2001–2002 has been examined a group of school children from City of Veles (n = 203 with average age x = 10.06). In Veles have been registered high blood lead levels x = 37.27 μg/dl with the range of 89.98 (2.57–92.55 μg/dl). There have not been found lead line in the gum of the investigated children.

In June 2003, has been investigated group of schoolchildren living in Veles (n = 31 at the 12.8 age) – polluted central area of the city near to the Lead Smelter Plant (1 km distance on the southwest). They have been educated in the Primary School “Vasil Glavinov”. There have been registered increased blood-lead levels in the examinees, as a result of the lead exposure from the Lead Smelter Plant (n = 31, x = 16.51 μg/dl with a range of 8.1–32.9 μg/dl). There have been registered lower blood-lead levels in the examinees, compared to the situation in 2001–2002 as a result of 20 days without emission from the Lead Smelter Plant. There was a high significant statistical difference between the blood-lead levels in the examined schoolchildren in 2001–2002, and schoolchildren in June 2003 (Student t-test $t = -6.37$ $p < 0.0001$). The difference can be explained by stop of working of the Lead Smelter Plant, and biological lifetime of lead into blood and soft tissues. This is a confirmation that there was an exposure of the children to the ambient air’s lead and there was a high environmental-health risk.

In 2004 was performed new investigation of schoolchildren’s blood-lead levels (n = 93, x = 7.64 μg/dl, with a range of 0.75–21.4 μg/dl). One year time distance without emission to the lead in the ambient air has shown significant decrease of average annual concentration of lead in the ambient air in 2004 in Veles (x = 0.15 μg/m^3), followed by significantly lower blood-lead levels in the examined schoolchildren compared between 2003 and 2004 (Figure 3). There was found very high significant statistical difference between the blood-lead levels in the examined schoolchildren in 2001–2002, and schoolchildren in 2004 (Table 2).

The average values of blood-lead levels in schoolchildren were significanthly higher in 2001–2002 and 2003, than the recommended value of 10 μg/dl proposed by Guidelines for Air Quality (WHO, 2000).

TABLE 2. Annual distribution of blood-lead levels in schoolchildren in Veles, μg/dl.

Year of investigation	Number of examinees	Average blood lead level	SD	Minimum	Maximum
2001–2002	203	37.27	17.93	2.57	92.55
2003	31	16.51	6.74	8.1	32.9
2004	93	7.64	4.39	0.75	21.4
WHO recommended value = 10					

Student t-test $t = 6.37$ $p < 0.001$ (2001–2002 compared to 2003).

Student t-test $t = 15.71$ $p < 0.001$ (2001–2002 compared to 2004).

Student t-test $t = 8.43$ $p < 0.001$ (2003 compared to 2004).

Using Spearman Rank Order Correlations have been found negative correlations between the average annual concentrations of lead in the ambient air in 2001, compared to schoolchildren’s blood-lead levels ($r = -0.17$ $p < 0.05$), as well in 2003 ($r = -0.12$ $p < 0.05$), and in 2004 ($r = -0.09$ $p < 0.05$). From the figures it could be concluded that correlations was quite higher during working of the Lead Smelter Plant in 2001 and first half of 2003, compared to 2004 when this Plant has not worked.

Hilts (2003) performed longitudinal study in Treil, British Columbia of blood-lead levels in pre-schoolchildren, from 1998–1996. The average blood-lead levels have decreased by the average range 0.6 μg/dl per year. From 1996–1999 the average blood-lead levels have decreased by the average range of 1.8 μg/dl annually, from 11.5 μg/dl in 1996 to 5.9 μg/dl in 1999. Recent fast drop was due to start of work of new Lead Smelter Plant with flash-smelting technology. In 1998, the average annual ambient air level was 0.28 $\mu g/m^3$, compared to 1.1 $\mu g/m^3$ in 1996. During summer 2001, Lead Smelter Plant has not worked for 3 months, and the average ambient air level decreased to 0.03 $\mu g/m^3$. The average blood-lead level in pre-schoolchildren dropped to 4.7 μg/dl.

Wang et al. (1998) have performed a study in a Plant for battery recycling, and found out that 31 from 64 workers have suffered by lead poisoning. Children that were going to the kindergarten in the vicinity have shown higher blood lead levels (15–25 μg/dl), and moderate decreasing of IQ (Binet-Simon scale), compared to children that were not exposed from socio-economic comparable kindergarten. Indoor air samples from the kindergarten have recorded average value more then 10 $\mu g/m^3$. Samples of soil have recorded 400 fold higher content of lead, which was lowering if sample has been taken from

15–30 cm (depth), or 350 m away from the Plant for battery recycling. Follow-up investigation 2.5 years later, after moving out of children away from the source of pollution, has been shown considerable decreasing of blood lead levels of children and partial recovery of their IQ.

5. Conclusion

There was statistically high significant difference by Student t-test of the average annual concentration of lead in the ambient air in Veles in 2001 (x = 0.94 µg/m^3), compared to the 2003 (x = 0.22 µg/m^3). Registered average annual concentration of lead in the ambient air in 2001 was 89% higher than the recommended value from WHO and EU (0.5 µg/m^3). Increased concentration of lead in the ambient air, represent high risk factor for the health of the exposed children population in the city of Veles.

In the frame of the study during 2001–2002 has been examined a group of school children from the City of Veles (n = 203 with average age x = 10.06. In June 2003 have been performed a control study on group of schoolchildren living in Veles (n = 31 at the 12.8 age) – polluted central area of the city near to the Lead Smelter Plant (1 km distance on the southwest). There have been registered lower blood-lead levels in the examinees, as a result of 20 days without emission from the Lead Smelter Plant (n = 31, x = 16.51 µg/dl, with a range of 8.1–32.9 µg/dl).

There was a very high significant statistical difference between the blood-lead levels in the examined schoolchildren in 2001–2002, and schoolchildren in June 2003. The difference can be explained by stop of working of the Lead Smelter Plant, and biological life-time of lead into blood and soft tissues. This is a confirmation that there was an exposure of the children to the ambient air's lead and there was a high environmental-health risk. In 2004 as a fact on stopping of ambient air emission by lead the blood-lead levels in schoolchildren have significantly dropped (n = 93, x = 7.64 µg/dl) with very high significant statistical difference between the blood-lead levels in the examined schoolchildren in 2001–2002, and schoolchildren in June 2004. There was a very high significant statistical difference between the blood-lead levels in the examined schoolchildren in 2003, and schoolchildren in June 2004. This trend of improvement was not significantly followed relating to annual ambient air concentrations of lead in 2003, compared to 2004. Regarding the figures concerning the blood-lead levels during years of working of the Lead Smelter Plant in 2001–2003, and without it in 2004, it was shown significant decrease of blood-lead levels. This fact is mainly contributed to the stop of emissions of lead in the ambient air from the Lead Smelter Plant in second half of 2003, and only 2–3% to the decreasing of use of leaded gasoline in the urban traffic of Veles. In autumn

2003 has started the "Campaign for phasing-out of leaded gasoline" in the Republic of Macedonia.

Recommendation

It can be assumed that the increased ambient air lead levels represent a risk factor for the exposed population and the recommendation is that the annual average lead level should be lower than the 0.5 $\mu g/m^3$, in order to avoid the impact to adverse health effects into humans, especially children as a most vulnerable group. With a goal to prevent adverse health effects of vulnerable group of population have been recommended environmental health measures and program for recovery. Program for monitoring of the environmental pollution by heavy metals and recovery, and environmental health impact assessment has been started since 2004, and it continued till the end of 2005. Ministry of Health and Ministry of Environment and Physical Planning in cooperation with the Republic Institute for Health Protection-Skopje, Institute for Health Protection-Veles, Institute for Occupational Diseases-Skopje, Clinical Centre-Skopje, Medical Centre-Veles and Local Authorities were working in finding the best solutions in order to reduce pollution from the past, and to prevent any further contamination of the region.

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EVALUATION OF THE RISK OF UNDERGROUND WATER'S ACTION UPON HUMAN HEALTH OF POPULATION IN MUNICIPALITY CHISINAU

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Abstract. There were presented the hygienic evaluation of drinking water quality from wells used for drinking propose by the population from mun. Chisinau. It was studied the correlation between the indices of water quality and morbidity of population and was calculated chemical risk. The used of the non qualitative drinking water direct influenced the human health of population.

Keywords: drinking water, chemical indices, correlation, morbidity of population, chemical risk

1. Introduction

WHO had proposed in 1977 the strategy entitled "Health for everyone", which had the aim that all citizens of the world accomplish a level of health that would allow them to have a productive social and economical life. Human health protection is one of the principles of long social and economical development stipulated in *the Strategy of Economical Increasing and Poverty Reducing* UN's initiatives for *Millenary Development* (Results of survey of health status…, 2006). Directions of this strategy were the main point in elaboration of National Polity of Health, recently approved by the Government in Republic of Moldova (Politica Națională de Sănătate, 2007).

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2. Aim

The evaluations of general morbidity particularities of population and water quality used for drinking purposes by the population of mun. Chisinau.

3. Material and Methods

It was studied the results of laboratory investigation of water of 350 wells from 18 rural places from municipality Chisinau in the period 2003–2006. At the evaluation of the water quality we used the norms of State Standard "The demands for water quality at underground sources. Protection of the sources" Nr. 06.6.3.18–96 from 23.02.1996. Per total there were analyzed about 8,000 samples of water. To study the role of water and its influence on human health we used the method "Risk Assistant" proposed by USA Agency for elaboration of technologies environment's protection (California Environmental Protection Agency, 1996; USEPA, 1997).

4. Results

The majority of the population from municipality Chisinau, resident in rural place, use drinking water from wells (about 51.8%). The total number of wells and springs from Chisinau is 1,730. The results of investigations show that 84.5% ± 5.34% of samples don't correspond to existing rules for the chemical indices and 65.8 ± 9.35 for the microbiological indices.

It was revealed increased concentration of nitrates in 84.6% ± 2.59%, hardness in 58.8% ± 3.8%, total dissolved solid – 35.3% ± 4.15%, sulfate – 12.5% ± 2.83% and ammonia – 3.6% ± 1.15% (Table 1).

TABLE 1. The frequency of determination of water samples that don't correspond to hygienic demands, average level, 2003–2006 years.

Place	Total nonstandard samples	Inclusive					
		Nitrate	Hardness	Total dissolved solid	Sulfate	Chloride	Ammonia
	M ± m	M ± m	M ± m	M ± m	M ± m	M ± m	M ± m
Average level, mun. Chisinau	84.3 ± 2.05	80.6 ± 2.59	58.8 ± 3.80	35.3 ± 4.15	12.5 ± 2.83	3.6 ± 1.15	0.1 ± 0.11
Urban place	86.5 ± 2.01	61.9 ± 2.72	48.5 ± 3.60	31.3 ± 4.36	0.7 ± 2.89	0	0
Rural places	84.2 ± 1.94	81.7 ± 2.68	59.4 ± 3.63	35.5 ± 3.92	13.1 ± 2.76	3.8 ± 1.11	0.1 ± 0.11

We have to mention that in five suburb places Durlesti, Codru, Stauceni, Ghidighici and Cricova from total samples a number of 90% had exceeded the hygienic norms. All samples from all places have corresponded to hygienic demands after organoleptice indices. The consumer doesn’t realize the risk of the water, described here, upon his health and the necessity of taking prophylactic measures in order to improve the system of water supply (Opopol and Russu, 2006; Friptuleac et al., 2006). The incidence of general morbidity in Chisinau was 38,349.0$\%_{00.}$ There were not a significant difference between the morbidity from rural place and towns: 3,845.6 versus 3,884.2 cases per $\%_{00.}$ The most spread diseases of the population during the studied period were respiratory, circulatory, digestive and urinary system (Table 2).

TABLE 2. General morbidity of population from mun. Chişinău ($\%_{00}$).

Grupe of diseases	mun. Chişinău	Inclusively	
		Towns	Rural places
1	*2*	*3*	*4*
Circulatory system’s diseases	7,655.9	7,688.9	7,312.3
Respiratory system diseases	8,216.5	8,570.0	4,532.3
Cancer	641.9	632.9	736.1
Congenital anomalie	376.2	374.1	397.4
Mental diseases	576.5	590.5	429.6
Central nervous system diseases	668.8	621.4	1,162.8
Blood system diseases	1,029.7	1,040.7	915.0
Endocrine diseases	2,437.9	2,430.8	2,511.7
Digestive systems diseases	5,626.8	5,531.6	6,618.8
Chronic hepatitis, cirrhoses	860.6	761.6	1,891.5
Obesity	472.3	461.2	588.0
Malnutrition	54.9	39.8	212.6
Endemic diseases	63.8	56.7	137.8
Urinary diseases	4,434.2	4,454.1	4,227.3
Alcoholism	839.4	805.7	1,190.6
Alcoholic psychosis	29.8	28.6	42.5
Other types of narcomanies	533.4	573.4	117.3
Diseases of pregnant women	1,451.8	1,425.4	1,727.3
Premature deliveries	20.5	20.0	26.4
Diseases of newborns	139.9	121.4	332.8
Neuromuscular system diseases	1,481.7	1,427.5	2,046.9
Trauma lesions and poisoning	736.4	689.3	1,227.3
Total	38,349.0	38,345.6	38,384.2

Analyzing the water quality and morbidity of population from Chisinau we revealed that the quality of water directly leads to digestive diseases, chronic hepatitis, cirrhoses, urinary diseases and endemic diseases (fluorosis, endemic goiter). The correlation index was 0.89 for endemic diseases, 0.83 for urinary diseases, 0.72 for chronic hepatitis and cirrhoses, 0.69 for digestive diseases.

The hygienic evaluation of the risk, using the methodology “Risk Asisstant”, established that in all places of the mun. Chisinau the relative chemical risk had a value over 1.0 and varied in range 41.55 in locality Vatra to 11.58 in locality Revaca.

5. Conclusions

1. The quality of the water from the mun. Chisinau wells and springs don’t correspond drinking conditions on chemical indices.
2. The level of morbidity of population living in rural places, in special, of chronic hepatitis and cirrhoses, traumatism, alcoholism, neuromuscular system diseases, digestive system diseases are high in comparison with urban places habitants.
3. The unfavorable quality of the water directly influenced the human health of the population from mun. Chisinau.
4. To improve the situation there are necessary to supply the rural population with drinking water in accordance with establish standards, which can be realized with common state actions.

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Rezultatelestudiului asupra sănătății populației în Republica Moldova = Results of survey of health status of population in the Republic of Moldova/ *Biroul Naț. de Statistică al Rep. Moldova. – Ch.: Statistica, 2006 (tipogr. SA “CRIO”), 286 p.*

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OCCURRENCE AND ASSOCIATED RISK OF NITRATES/NITRITES IN THE GROUND WATERS FROM THE NORTH-EASTERN PART OF ROMANIA

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Abstract. The presence of nitrates/nitrites at high concentrations in groundwater resources represents an important issue for human health and a great environmental risk. The purpose of this study is to present an analysis of data collected by monitoring nitrates/nitrites concentrations in six counties from the North-Eastern region of Romania and to asses the risk associated with their presence. The research was conducted over 1 year (2007), taking samples from drinking water and groundwater resources (4–5 sources from every county). This study has been accomplished with the support from "Transports, Constructions and Tourism Minister" network, from the North-Eastern region of Romania. An overview of the risk zones has been made and suggestions over the necessary water treatments are presented.The secondary objective of this study was also the creation of a monitoring data base of nitrites/nitrates, which will contribute into taking the adequate integrated pollution prevention and control measures.

Keywords: nitrites/nitrates, groundwater, risk zones, risk assessment

1. Introduction

Nitrates can be of natural and synthetic origin. Nitrate is an important metabolite in the biological nitrogen cycle, produced during nitrification of reduced

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nitrogen compounds. It is a natural constituent of soil and vegetation and also a normal metabolite in mammals. Nitrate in soil, ground and surface water derive mainly from mineralization of soil organic matter; some also from application of mineral fertilizers. The major natural deposit of nitrates is that of sodium nitrate (Chilean saltpetre) in northern Chile. Nitrates are produced on a large scale from nitric acid made from ammonia by catalytic oxidation. Nitrates are formed from the reaction of nitric acid with ammonia or minerals (e.g. phosphate rock) to give ammonium nitrate and water soluble salts used as fertilizers (www.inchem.org).

TABLE 1. Transformation pathways of nitrates/nitrites into the human body.

Nitrites/nitrates transformations in human body	Description
Absorption	Nitrate and nitrite given orally are absorbed and transferred to the blood in the upper part of the gastrointestinal tract Abundant pectin in the food may delay absorption which may then occur lower down in the intestine, with possible increased risk for microbial transformation of nitrate into nitrite
Distribution	Regardless of route of exposure, nitrate and nitrite are rapidly transferred into the blood. Nitrite is gradually oxidized to nitrate which is readily distributed into most body fluids (urine, saliva, gastric juice, sweat, ileostomy fluid). Distribution of nitrate into plasma, erythrocytes, saliva and urine following an oral dose of sodium nitrate has been demonstrated by Cortas and Wakid (1991)
Biological half-life reaction	Wagner et al. (1983) showed the half-life in the body for an oral dose of nitrate to be approximately 5 h. As blood absorption depends on food matrix and route of exposure, and as larger doses may increase the urinary excretion rate, the biological half-life for both nitrate and nitrite should be expected to be 3 to 8 h. Nitrate does not accumulate in the body
Metabolic reactions	Where bacteria are present and the environment can be anaerobic, nitrate can be reduced to nitrite. The main site for this reaction is mouth and stomach, but nitrite formation in the lower intestine and in the bladder (urinary infection) may also be of some toxicological importance Nitrite may be further reduced to nitrogen by bacteria under some conditions. In blood, nitrite transforms

	haemoglobin to methaemoglobin and is simultaneously oxidized to nitrate. Normally methaemoglobin gradually reverts to haemoglobin through enzymatic reactions Nitrite has vasodilating properties, probably through transformation into nitric oxide (NO) or a NO-containing molecule acting as a signal factor for smooth muscle relaxation Nitrite easily transforms into a nitrosating agent in an acidic environment and can react with a variety of compounds, e.g. ascorbic acid, amines, amides Nitrosation can also be mediated by bacteria, e.g. in the stomach. Some reaction products are carcinogenic (e.g. most nitrosoamines and amides
Elimination	Approximately 60% of oral nitrate is excreted in urine (Wagner et al., 1983). The fate of the rest is not completely known, but bacterial or endogenous metabolism probably accounts for the remainder. A minor part is excreted in sweat

The major use of nitrate is as fertilizer. It is also used in the manufacture of nitrites, nitrous oxide, explosives, pyrotechnics, matches, freezing mixtures and special cements. It is also used as a colouring and preserving additive to food, for coagulation of latexes, in the nuclear industry and for odour (sulphide) and corrosion control in aqueous systems.

Nitrite is also a metabolite in the biological nitrogen cycle, an intermediate in both nitrification and denitrification. It is also a normal metabolite in mammals. Nitrites in commercial use are all of synthetic origin. They are made mainly by dissolving nitrogen oxides (NO and NO_2) in alkaline solutions. Nitrites can also be prepared by reduction of nitrates.

Nitrite is used as a food preservative and colouring agent, e.g. curing of meat, in the manufacture of diazo dyes and rubber, in the textile industry and in photography. Nitrite is also used in analytical and preparative chemistry, as a corrosion inhibitor and as an antidote in cyanide poisoning.

The major concerns of nitrate and nitrite are associated with intake of food and water. Drinking water contains variable amounts of nitrate. The statutory limits can vary slightly from country to country, but usually maximum admissible concentration (MAC) is 50 mg NO_3^-/L in the EU. The transformations of nitrates and nitrites into the human body can take place through various ways, shown in Table 1.

2. Toxicology and Toxicity

2.1. TOXICOLOGICAL EFFECTS

The main toxicological concerns of nitrates are associated with its conversion to nitrite before or after reaching the human body. The major acute toxic effect is the development of methaemoglobinaemia, a condition where more than 10% of the haemoglobin is transformed into methaemoglobin, a stable compound that blocks the haemoglobin. When the conversion exceeds 70% the condition can be fatal. Nitrite may also cause sudden fall in blood pressure due to its vasodilating properties. These effects are reversible.

The major concern of possible long-term effects of exposure to nitrate and nitrite is associated with formation of nitroso compounds, many of which are carcinogenic (Wright and Welbourn, 2002). This formation may take place wherever nitrite and nitrosable compounds are present, but it is favoured by acidic conditions or the presence of some bacteria. The gastrointestinal tract and especially the stomach are regarded as the main formation site, but nitrosation reactions can also take place in an infected urinary bladder. Nitrosation reactions also occur elsewhere in the body as a result of endogenous formation of nitric oxide and nitrite, but the relative contribution of this source is presently unknown.

2.2. TOXICITY OF NITRATES/NITRITES

The toxicity of nitrates and nitrites has been studied on humans (and especially on neonates) and on animals.

As far as **adults** are concerned, the lethal oral dose of potassium nitrate for an adult has been estimated to be between 4 and 30 g (about 40 to 300 mg NO_3^-/kg). It has been reported that adults have tolerated large doses of nitrate as sodium and ammonium salt (> 100 mg NO_3^-/kg) in some cases repeated for several days for medical or experimental purposes with only minor effects in some subjects (light methaemoglobinemia, diarrhoea, vomiting). Death and severe effects of nitrate ingestion are generally associated with doses above 10 g NO_3^-. Doses between 2 and 9 g NO_3^- have been reported to cause methaemoglobinemia. These values correspond to 33 to 150 mg NO_3^-/kg (Walker, 1990).

The lethal oral dose of nitrite for adults has been variously reported to be between 0.7 and 6 g NO_2^- (approximately 10 to 100 mg NO_2^-/kg) (WHO, l985a; Corre and Breimer, 1979; Fassett, 1973; De Beer et al., 1975). Lower doses may apply for children (especially neonates), the elderly and people with certain enzyme deficiencies. The broad range is due to the wide variability in individual sensitivity. Human volunteers given sodium nitrite intravenously produced a maximum methaemoglobin level of 7% after a dose of 2.7 mg NO_2^-/kg and 30% after a dose of 8 mg/kg (Kiese and Weger, 1969). The first symptoms of oral nitrite poisoning develop within 15 to 45 min (ECETOC, 1988).

As far as **children** are concerned, the neonates are at special risk for high nitrate and nitrite levels as their enzyme system for regeneration of haemoglobin is not fully developed. Most clinical case data refers to neonates developing methaemoglobinemia after drinking water or water-based formulations with high nitrate or nitrite content. The great majority of cases (well-water methaemoglobinemia) occurred, when nitrate levels in drinking water exceeded 100 mg NO_{3-}/L (Bockman and Bryson, 1989). It is generally acknowledged that water nitrate content of 50 mg/L is safe even for neonates. Assuming normal liquid intake of 150 mL/kg/day by neonates, nitrate intake of 7.5 mg NO_3^-/kg/day is safe. Experiments indicate that even twice the amount is safe, but at a higher intake can cause methaemoglobinemia.

2.2.1. *Relevant Data on Animal Tests*

Animal experiments are difficult to evaluate and use for assessing the toxicity of nitrate in man because the toxic doses of nitrate and nitrite depend upon competing processes, the rates of which are not necessarily the same for man and animals.

Thus the kinetics of nitrite formation from nitrate, and the rates of haemoglobin regeneration are not necessarily comparable between animals and humans (ECETOC, 1988). This is especially so for ruminants where ingested nitrate is reduced in the rumen.

Lethal dose 50% (LD50) values for nitrate in rodents varies between 1.2 and 6.6 g NO_3^-/kg.WHO (1974) and JECFA (1980) considered 365 mg NO_3^-/kg as the highest daily dose over lifetime without adverse effects in rats. On this basis the acceptable daily intake (ADI) (given by WHO/FAO) is set. LD50 values for nitrite in rodents varies between 57 to 157 mg NO_2^-/kg. WHO (1974) concluded from long-term studies, that the level causing no toxicological effect was less than100 mg $NaNO_2$/kg/day (=67 mg NO_2^-/kg/day).

2.2.2. *Acceptable Daily Intake (ADI)*

The acceptable daily intake for nitrates (total for potassium and sodium nitrate) is up to 5 mg/kg, which corresponds to maximum 3.65 mg NO_3^-/kg (FAO/WHO, 1985b). Walker (1990) suggests that this value should be changed to 18.5 mg NO_3^-/kg, based on a more recent study.

The guideline value given by WHO (1984) for maximum concentration of nitrate in drinking water is 10 mg nitrate (as N)/L (= 44.3 mg NO_3^-/L) (WHO, 1984).

The acceptable daily intake for nitrites (total for potassium and sodium nitrite) is up to 0.2 mg/kg, which corresponds to maximum 0.13 mg NO_2^-/kg (FAO/WHO, 1985a). Walker (1990) suggests this value be changed to 0.07 mg NO_2^-/kg based on a more recent study. These values are not applicable to neonates. WHO makes no specific recommendations for maximum nitrite concentration in drinking water, but in the European Union the statutory maximum concentration is 0.1 mg NO_2^-/L (EEC, 1980).

2.3. CARCINOGENICITY

There is no evidence that nitrate or nitrite as such cause cancer in animals (ECETOC, 1988). However, a causal connection between nitrate/nitrite and cancer through the formation of N-nitroso compounds is suspected.

The role of nitrate and nitrite in the aetiology of cancer in humans, especially gastric cancer, is addressed in numerous studies which are reviewed and discussed by Walker (1990), Forman et al. (1989), ECETOC (1988), IARC (1987) and WHO (1985). Included are also epidemiological studies seeking to find correlation between frequency of cancer and nitrate intake with food and water. Evidence from these sources does not support the hypothesis of a straightforward cause and effect association between nitrate exposure and cancer risk (Forman et al., 1989).

2.4. TERATOGENICITY AND MUTAGENICITY

Studies relating congenital malformations and cardio-vascular effects to nitrate levels in drinking water have not produced consistent results (WHO, 1985; Black, 1989).

Nitrates show no mutagenic activity in microbial tests under aerobic conditions. Activity has been reported under anaerobic conditions, probably due to reduction of nitrate into nitrite. Mutagenic activity in vivo of high doses of nitrate is difficult to evaluate because of the possibility of chemical reduction.

Nitrite is mutagenic in a number of in vitro assays against microorganisms or cultured mammalian cells. Mutagenic effects were also observed in an in vivo and in vitro experiment using Syrian hamsters. In vivo assays have been equivocal, both positive and negative results having been reported (Walker, 1990).

3. Materials and Methods

There are several methods of determination of nitrates and nitrite in water, found in the literature, but the method chosen in this case has the advantages of being simple and very sensitive.

Materials needed in order to make the analyses are (Ballance, 1996):

- Water samples from drinking water and groundwater resources
- Reagents: stock potassium nitrates solution, hydrochloric acid diluted 1:4, sulfanilic acid, zinc mixed with natrium chloride, N-1-naphthylethylenediamine dihydrocloride, sodium acetate solution
- Distilled water
- Jasco UV-VIS 530 spectrophotometer

Determination method: The samples were taken from each prelevation point at each two months, over a period of 1 year (2007). There were a total of 102 samples from all the counties from North-Eastern part of Romania and from all the risk zones of each county. The counties are: Suceava, Botosani, Neamt, Iasi, Bacau and Vaslui (Figure 1).

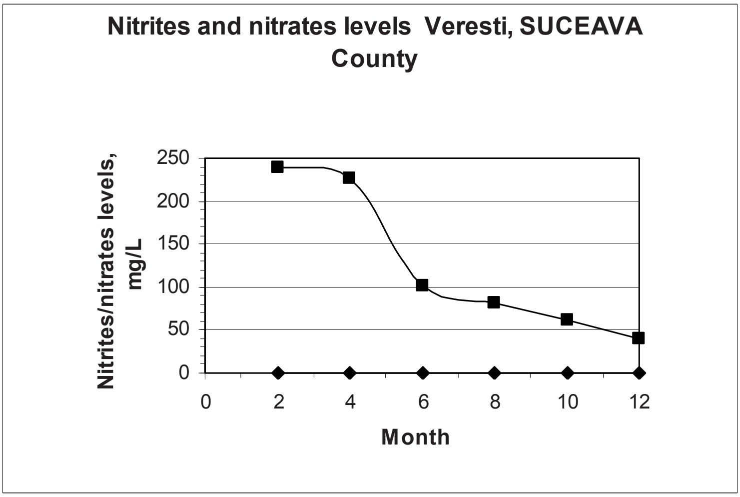
In our experiments, nitrates are reduced to nitrite with zinc. The nitrite reacts with sulfanilic acid and N-1-naphthylethylenediamine to produce a red compound. The intensity of the red color is analyzed spectrophotometrically. The color intensity was measured at a wavelength of 550 nm, and from the curve representing color intensity-concentration, the values of nitrites and nitrates concentrations have been obtained.

Figure 1. Counties from Romania in which the study was performed.

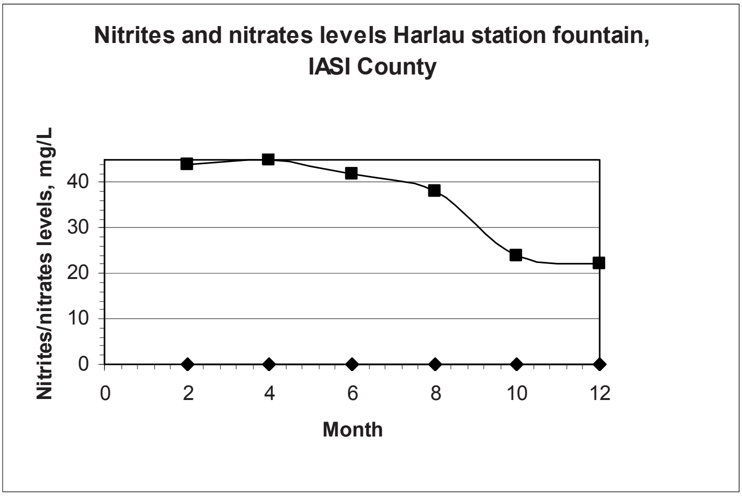
4. Results and Discussions

The results obtained were processed as graphs and some of the 2-month averages of nitrates/nitrites concentrations are presented in Figure 2a to f (the representatives ones in which nitrites/nitrates concentrations are maximum).

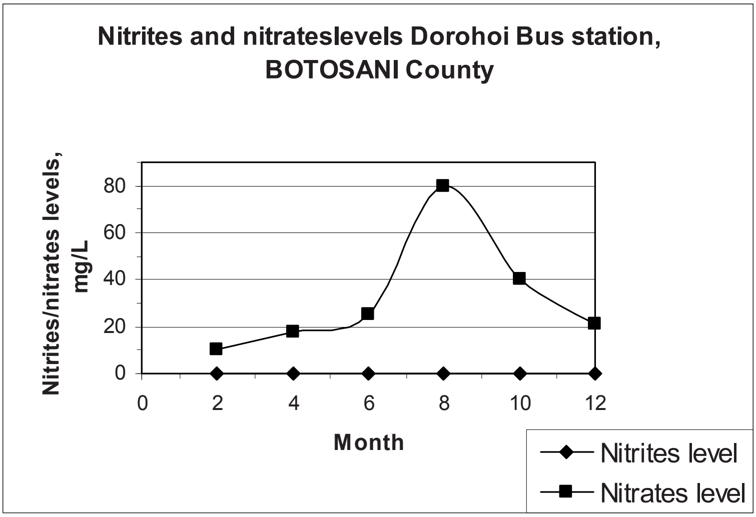
(a)



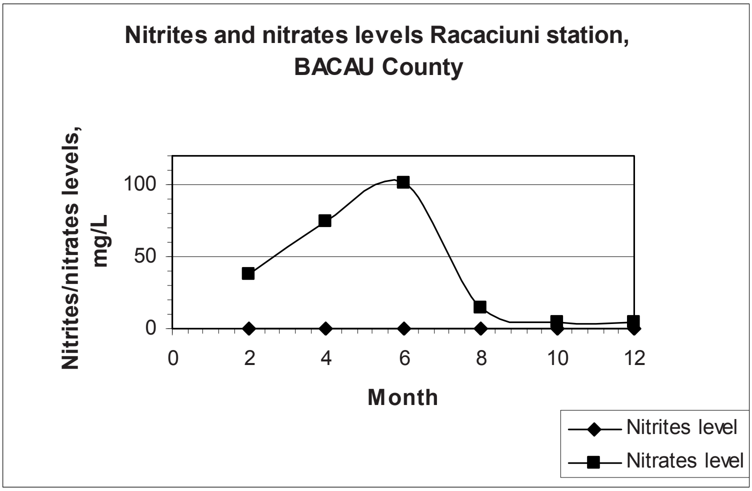
(b)



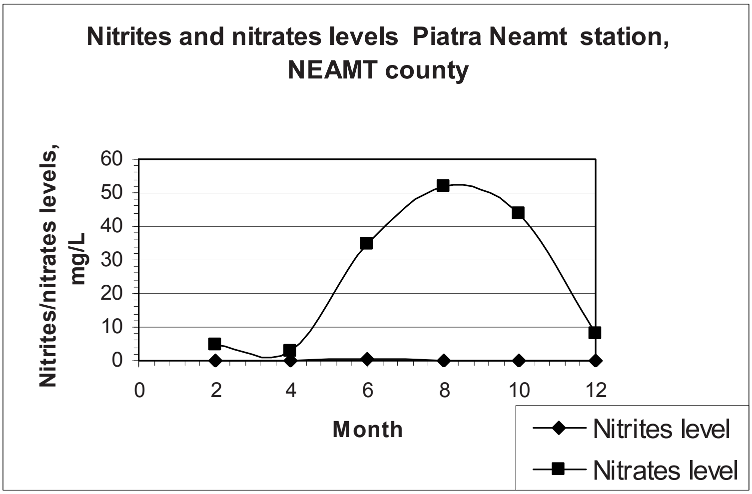
(c)


Nitrites and nitrateslevels Dorohoi Bus station, BOTOSANI County
Nitrites/nitrates levels, mg/L
0
20
40
60
80
0
2
4
6
8
10
12
Month
Nitrites level
Nitrates level

(d)


Nitrites and nitrates levels Racaciuni station, BACAU County
Nitrites/nitrates levels, mg/L
0
50
100
0
2
4
6
8
10
12
Month
Nitrites level
Nitrates level

(e)



(f)

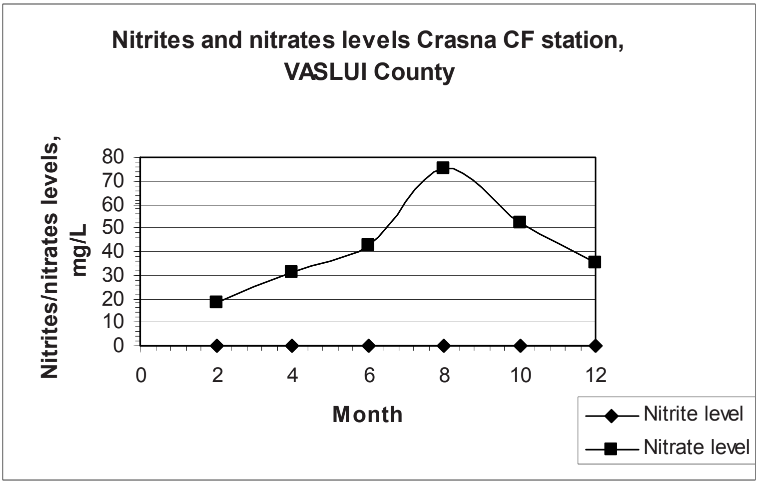


Figure 2. Two-month averages of nitrates/nitrites concentrations for SUCEAVA county (**a**), IASI county (**b**), BOTOSANI county (**c**), BACAU county (**d**), NEAMT county (**e**) and VASLUI county (**f**).

The results obtained were processed as graphs and some of the 2-month averages of nitrates/nitrites concentrations are presented in Figure 2a to f (the representatives ones in which nitrites/nitrates concentrations are maximum.

In Table 2, the results of the graphs show the maximum concentrations of nitrates found in the highest risk zone of each county. As far as nitrites are concerned, it may be concluded that none of the samples taken registered a value higher than the maximum admissible concentration (0.5 mg/L).

TABLE 2. Concentration of nitrate in each studied county.

County	Concentration of nitrate, mg/L
Suceava, Veresti	250*
Botosani, Dorohoi	80*
Neamt, Piatra Neamt	50*
Iasi, Harlau	45*
Vaslui, Crasna	75*
Bacau, Racaciuni	50*

* This value represents a 2 month average.

As it can be seen from Table 2, in almost every county the maximum admissible concentration (50 mg/L) was exceeded. The maximum value registered is five times higher (in Veresti, Suceava County). Top average values of nitrates are present in Botosani (52.5 mg/L), Vaslui (45.33 mg/L) and Suceava (43.75 mg/L), exceeding the alert value (38.5 mg/L).

In the summer time, in almost all of the considered counties, the level of nitrates registers a significant increase. This happens because of intensive agriculture, use of synthetic and non biodegradable fertilizers, inefficient sewerage systems and meteorological and hydrological position of each zone and county.

In Suceava and Bacau are recorded the highest values of nitrate percentage cases (50%, and 20%) which exceed the maximum admissible concentration (55 mg/L), as shown in the following graphic (Figure 3).

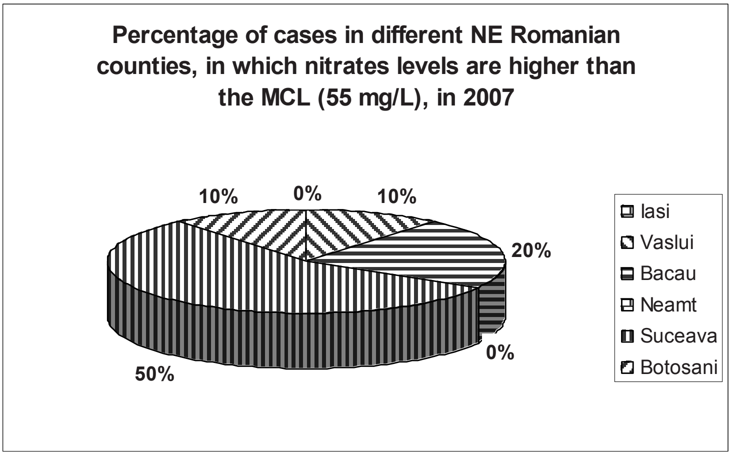


Figure 3. Percentage of nitrates/nitrites concentrations exceeding 55 mg/L, in different counties.

In order to realise a risk assessment on nitrates and nitrites found in groundwater resources, such as in our case, one can use decisional trees, as shown in the following graphics (WHO, 2004). The first graph (Figure 4) represents actions required in the event of detecting high nitrate concentrations in drinking water supply – for example groundwater. The second decision tree (Figure 5) presents a series of actions required in the event of detecting high nitrate concentrations in the drinking water supply of populations likely to suffer from associated health problems. This kind of approach can offer a complex image of the problem and can provide short and long term solutions, in order to eliminate the environmental risk associated with nitrites and nitrates. Once these results are obtained the next step is applying the necessary treatments needed for the elimination of these pollutants such as: **ion exchange denitrification**, **biological denitrification**, **a combination** of the previous **two processes** (van der Hoek and Klapwijk, 1987), **membrane separations** (electrodyalisis) (Reddy and Lin, 2000), **catalytically methods**, but ion exchange denitrification remains the first option in the case of groundwater (WHO, 2004; Kapoor and Viraghaven, 1997). The final step would be to further monitor the situation, to prevent the occurrence of the same or worse situations.

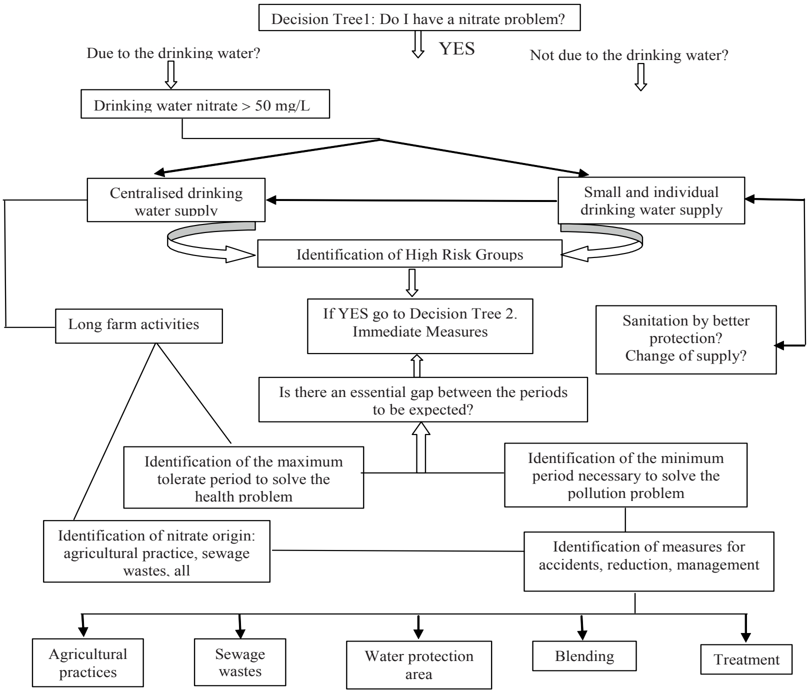


Figure 4. Actions required in the event of detecting high nitrate concentrations in drinking water supply – for example groundwater.

5. Conclusions

This study presented an overview of the risk zones contaminated with nitrites and nitrates and suggestions over the necessary water treatments are mentioned. It has been accomplished with the support from “Transports, Constructions and Tourism Minister” network, from the North-Eastern region of Romania The secondary objective of this study was also the creation of a monitoring data base of nitrites/nitrates, which will contribute into taking the adequate integrated pollution prevention and control measures.

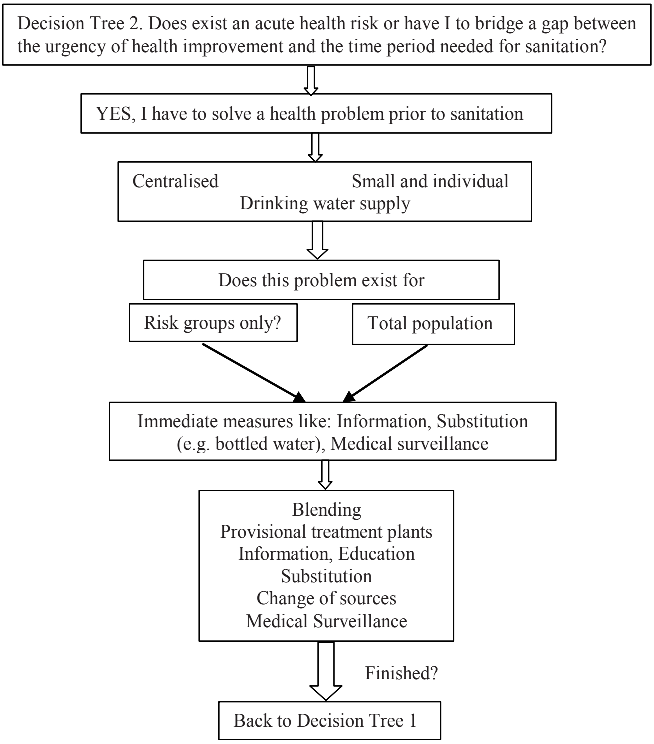


Figure 5. Actions required in the event of detecting high nitrate concentrations in the drinking water supply of populations likely to suffer from associated health problems.

It was observed that increased values were registered in almost every county and region of the county in which the study has been conducted. The most representative values were presented in this article. In Romania, the problem of nitrites and nitrates had a more severe impact because until recent years, water resources, especially groundwater, were not sufficiently monitored for contaminants. On one hand the environmental legislation was not adequately enforced and on the other hand people were not aware of the importance and necessity of water treatments. Nowadays in Romania, the European legislation has been adopted entirely and water quality is strictly controlled, in conformity with UE laws. For example, a project initiated in 2004 by ARA (Romanian Association of Water) has as main objective to repair the existent water alimentation systems and to create new ones in rural areas, until 2012. In the last decade, the population in Romania has become more and more concerned of the risk of consuming contaminated water from groundwater resources, so this kind of studies that monitor and asses the risk are welcomed and necessary.

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NEW TECHNOLOGIES FOR NITRITE AND NITRATE REMOVAL FROM DRINKING WATER ENVISAGING THE DIMINUTION OF HUMAN HEALTH RISK

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Abstract. The risk of nitrite and nitrate ingestion on human health comes from various sources, e.g., water, vegetables and meat produces. Nevertheless the maximum allowance concentration for nitrite and nitrate in drinking water is the smallest in comparison with vegetables and meat products, however water mainly contributes to human health risk because of the great exposure of the population to water ingestion. The treatment of natural zeolite with quaternary amines converted it into suitable compounds for retaining certain anions, i.e., nitrite and nitrate. Two types of organozeolites were used for the removal of nitrite and nitrate anions, namely DDAC (*distearyl – dimethyl – ammonium – chloride*), respectively SDBAC (*stearyl – dimethyl –benzyl – ammonium – chloride*). Two concentrations of quaternary amines, 100 and 200 mM were used to modify the zeolite. The organozeolite performances for the removal of nitrite and nitrate from water were determined.

Keywords: organozeolite, nitrite, nitrate, human health risk

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L.I. Simeonov and M.A. Hassanien (eds.), *Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology*,

1. Introduction

Given the pollution of the air, the quality of the water used by the population may be a significant factor that causes diseases. Besides diseases that are caused by different micro-organisms, water may influence the general health of human collectivities also by its contents of mineral elements that take an active part in vital processes (Vlaicu, 1998).

Among environmental issues that have an impact on the death of population caused by non-catching diseases, there is the chemical quality of drinking water. In this sense, it is commonly known that water has a very complex chemical composition that includes a large number of dissolved chemical elements. The natural composition of water includes various mineral substances that can also be found in the human body, macro-elements (salts of calcium, magnesium, natrium, potassium, chlorides, etc.), others in very small quantities, micro-elements (iodine, fluoride, chromium, selenium, vanadium, etc.). They are defined as biogenic substances, vital for the functioning of the body. Their excess disturbs this good functioning, by the possible appearance of public health issues. But water may be also polluted by toxic substances, like: nitrates, pesticides, detergents and heavy metals (Jacqmin and Commenges, 1996).

The health risks due to the presence of toxic chemical substances are different from the risks of microbiological contamination of drinking water. Without taking this issue too lightly, the chemical constituents from water rarely lead to acute effects, except for a massive accidental chemical pollution of a water source. It is the health problems caused by long and unwanted exposure to substances with cumulative toxic properties: heavy metals, cancer causing substances (Friptuleac et al., 1999).

The contamination with nitrates and nitrites of underground water sources is a serious problem in many regions, especially in the rural area. Agriculture has a major contribution to the deterioration of water quality due to the use of fertilizers and pesticides that infiltrate into the ground water. Consequently, water sources often contain toxic chemical compounds, with a risk concerning the health of the population. One can observe high levels of nitrates and other organic and microbiological polluters, in fountain waters. The increased concentration of nitrates and nitrites in well waters is also due to the polluting sources around the well (lack of hygiene, toilets located at reduced distances and depths of only 4–5 m, the disposition of animal stables up-hill as related to the drinking water source, etc.). After heavy rains periods, water infiltrates into the local sources of drinking water. Another reason of pollution is the fertilization of soils by nitrate fertilizers. There are in Romania a very large number of water sources that would have to be prohibited for use, but the lack of alternative solutions perpetuates the use of improper wells and springs (Iacob et al., 1999).

The various chemical substances dissolved in water may have significant effects on the health of living bodies in general and on human health in particular. A whole series of non-catching diseases are nowadays considered as being caused or favorized by the chemical composition of water, namely: endemic goiter, tooth decay and endemic fluorosis, heart diseases, methemoglobinemia, etc. Inside the mouth, nitrates turn into nitrites (phenomenon that accentuates in the case of small children due to the increased alkalinity of their saliva) and, in the bloodstream, it combines with the hemoglobin, forming methemoglobin. This phenomenon blocks the red cells of the blood and causes “cyanosis”, and, in the case of small children, it may even lead to death (“blue child” disease) (Burtica et al., 2005).

Along with the increase of environment nitrate and nitrite concentration, there has been observed an always increasing incidence of chronic intoxications with nitrates at small children (0–7 years old). Moreover, there is a major risk in the presence of nitrates and nitrites in vegetables in the rural area, with the possibility of forming nitroso-amines, substances that have a high cancer and mutant potential (Thomson, 2004).

Zeolite minerals have found an increased range of applications in the field of pollution control, based on their remarkable selectivity in adsorption and ion exchange (Cruceanu et al., 1986).

They are cage like structures with high exchange cations capacities. Clinoptilolite is the most abundant naturally occurring zeolite in Romania.

As a chemically modified ion exchange agent, there can be used the natural zeolite of the clinoptilolite type, chemically modified as organozeolite, in view to retaining inorganic anions from water. By altering the surface of the clinoptilolite with amines, a hydrophobic surface was obtained, which can retain inorganic anions (Vujanovic et al., 2003).

The treatments of clinoptilolite with quaternary amines make them to gain an affinity for inorganic oxyanions. The affinity is more intense with the length of carbon chain of amines (Lemic et al., 2005).

The aim of this study was to remove nitrite and nitrate anions from water by using Romanian zeolite modified with quaternary amines in order to reduce nitrites and nitrates’ risk on human health. Two types of quaternary amines were used to modify zeolite so as to become suitable for nitrite and nitrate removal form water, *distearyl-dimethyl-ammonium-chloride* (DDAC), respectively *stearyl-dimethyl-benzyl-ammonium-chloride* (SDBAC).

2. Materials and Methods

Starting from this fact, a study was initiated on reducing the loading of the polluted waters with nitrites by retaining them on organozeolites.

The laboratory research used natural zeolite from the NE of Yugoslavia with a content of 80–90% of clinoptiolite and a composition of: 69.95% SiO_2; 12.76% Al_2O_3; 1.25% Fe_2O_3; 2.80% CaO; 0.29% MgO; 0.45% Na_2O; 3.13% K_2O; 0.0194% MnO; 0.167% TiO_2.

In order to increase its affinity for the inorganic anions, the natural zeolite was modified with quaternary amine for: SDBAC type (*stearyl–dimethyl–benzyl–ammonium–chloride*) and DDAC type (*distearyl-dimethyl-ammonium-chloride*). These organozeolites were prepared by the Institute for Technology of Nuclear and Other Raw Minerals, Belgrade, Serbia. A quantity of 500 g of thermally treated (100°C for 2 h) zeolite was added to surfactant solution with desired concentrations (100–200 mmol/dm^3). The suspension was mechanically mixed for 30 min, then washed and dried at 70°C.

Comparative studies were carried out in order to remove nitrite and nitrate anions by using these modified zeolite, using nitrite and nitrate solutions with concentrations ranged between 0.46 and 552 mg * L^{-1}.

Two grams of each kind of zeolite (SDBAC and DDAC, 100 and 200 mM) were mixed with 8 ml of nitrite and nitrate solution. The samples were shacked at 25°C about 24 h, a period shown sufficient for retain the nitrite and nitrate ions on the zeolite modified with quaternary amine. When the time ran out, the suspension were filtrated and analyzed. To determine the nitrite and nitrate concentration in residual solutions the standardized Griess spectrophotometric method with GBC Cintra 5 spectrophotometer, was used.

3. Results and Discussions

This study was carried out to test the capability of zeolite modified with two concentrations of DDAC and SDBAC (100 and 200 mM) to remove nitrate and especially nitrite from water.

In Figure 1 are shown the results obtaining after 12 h of contact from solution with various concentrations of nitrate and zeolite modified with 100 and 200 mM DDAC.

As expected the better results related to the removal efficiency with DDAC with higher concentration (200 mM), was reached for the initial concentration of nitrate up to about 300 mg * dm^{-3}, the removal efficiencies are almost constant and the effiencies decreased beyond this concentration. Using zeolite modified with 100 mM DDAC the efficiency for nitrate removal reached maximum about 75%, and about 99% for 200 mM DDAC.

Figure 2 shows the results obtained for nitrite anion removal under the similar conditions mentioned in Figure 1. Also, the higher concentration of quaternary amine led to better results. Though, the efficiencies for nitrite removal over 80% was not reached.

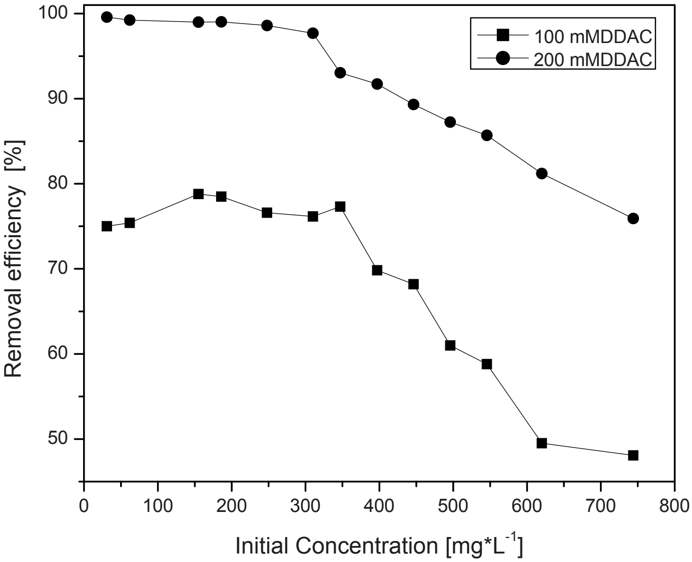

Figure 1. Nitrate removal efficiency using the zeolite modified with DDAC.

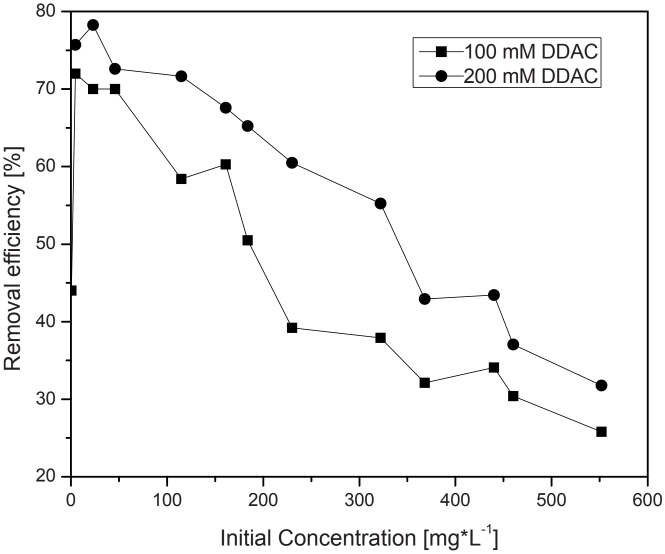

Figure 2. Nitrite removal efficiency using the zeolite modified with DDAC.

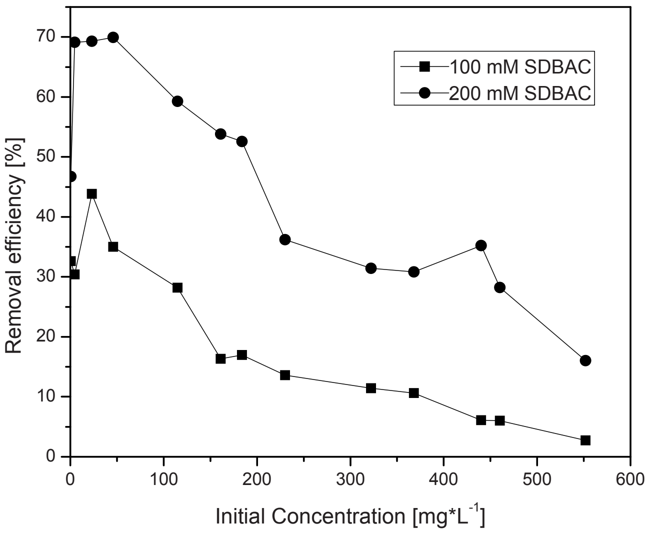

Figure 3. Nitrite removal efficiency using the zeolite modified with SDBAC.

In Figure 3 the efficiency for nitrite removal using SDBAC is shown. It can be noticed also the better efficiencies for higher concentration of SDBAC.

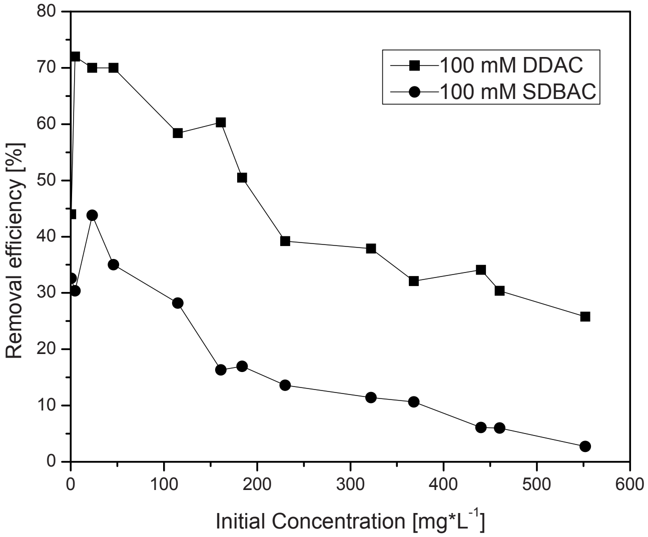

Figure 4. Nitrite removal efficiency using the two types of zeolite modified with 100 mM DDAC and 100 mM SDBAC.

Comparing the results obtained for quaternary amines, by using DDAC, the better results were reached.

Based on the presented results, it can be concluded that by using 100mM DDAC the very good performance of nitrate and nitrite removal process was achieved.

4. Conclusions

Modifying zeolite with two types of quaternary amines, e.g., SDBAC (*stearyl – dimethyl – benzyl – ammonium – chloride*) and DDAC (*distearyl–dimethyl–ammonium–chloride*) allowed their using for the removal of nitrite and nitrate anions from water.

The removal process of nitrite and nitrate from water depended on formed factors, i.e., the type of quaternary amine, the concentration of quaternary amine, the initial concentration of nitrate and nitrite ions. Under the studied conditions, the best results subjected to the removal efficiency was reached by using 200 mM DDAC. Also, the performance of removal process was better for nitrate than nitrite anion.

Acknowledgement: This work was supported by project CEEX – PROAQUA No. 631/03.10.2005 "Promoting innovative and sustainable technologies for drinking water treatment" and the project: PNII–ZEONANO–SPP No.56/ 14.09.2007 "Synthesis of functionalized zeolite materials with doped titanium dioxide nanoparticles and testing in water potabilization pilot stations".

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ABOUT THE CONTENTS OF NITRATES IN VEGETAL FOOD–STUFFS IN MUNICIPALITY OF CHISINAU

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Abstract. There were analyzed the results of laboratory investigations of samples of different vegetal food – stuffs for determination of nitrates made in the Center of Preventive Medicine of municipe Chisinau during the last 5 years (2003–2007). In general, the average parts of samples with increased quantities of nitrates were 8.8%; 5.9%; 2.2%; 5.9% and 6.4% in the years 2003, 2004, 2005, 2006 and 2007, respectively. Every year were established nitrates over norms in samples of radish, beet – roots, potatoes and autumn cabbage, during 4 years – in vegetable marrows and melons, during 3 years – in green onions and green grocery. Quantities of nitrates over norms never were revealed during the period of the study in fruits, grapes, mushrooms and different berries. It was proposed some recommendations.

Keywords: vegetables, nitrates, laboratory investigations

1. Introduction

Nitrate (NO_3) is an inorganic anion resulting from the oxidation of elemental nitrogen. It is an essential nutrient for plant protein synthesis and plays a critical role in the nitrogen cycle of soil and water. Nitrates are produced by natural biological and physical oxidations and therefore are ubiquitous in the environment (Ridder and Oehme, 1974). Most of the excess nitrates in the environment originate from inorganic chemicals manufactured for agriculture. Farmers often

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apply fertilizers in the form of ammonium or sodium nitrate in excess to their crops. When the concentration of nitrates in the soil is higher than the plants can use, the excess nitrates appear in the surface and ground waters and are often found in drinking water, especially in rural agricultural areas served by wells. In this conditions food – stuffs of vegetal origin can accumulate the nitrates in increased quantities (Opopol and Dobrianskaya, 1986). From the other hand, ammonia from animal waste and septic tanks can be oxidized to nitrate by soil bacteria under aerobic conditions. This can also be a significant source of nitrate in surface and groundwater especially near areas of concentrated animal populations, such as feedlots and dairy barns. The groundwater contamination also depends on different conditions – the type and thickness of the soil, the amount of precipitation, irrigation and others. High concentrations of nitrates in vegetables can reflect the over application of nitrate-containing fertilizers (Busuioc et al., 1997).

In the human organism inorganic nitrates can be reduced to nitrites (NO_2) by the microflora in saliva and the gastrointestinal tract. It is considered, that nitrites are responsible for most of the toxic effects observed with excess nitrate ingestion (Opopol and Dobianskaya, 1986; Johnson and Kross, 1990). Nitrites formed from nitrates by the microflora in the salivary ducts and gastrointestinal system are primarily responsible for the toxic effects observed after nitrate ingestion (Bouchard et al., 1992). An excess of nitrites produced by the reduction of organic or inorganic nitrates can oxidize the iron in hemoglobin from ferrous (2+) to ferric (3+), forming methemoglobin (Craun et al., 1981; Bouchard et al., 1992). This condition (methemoglobinemia) can lead to a lack of oxygen in tissues and is the primary toxic effect of inorganic nitrate ingestion. The infants less than 6 months old comprise the most sensitive population. Besides methemoglobinemia there are suspected different other unfavourable effects of these substances upon mammals and human organism, for example, a possible carcinogenic effect due the formation of nitrosamines, teratogenic effect, influence upon immune system and tissue enzymes, possible promotion of heavy metals' accumulation, for example, lead and cadmium (Ильницкий 2003; Митченков et al., 1997; Opopol and Dobrianskaya, 1986). That is why we put the task to analyze the real state concerning the contents of nitrates in food – stuffs or vegetal origin, one of sources of these substances for human organism, during the 5-year period of time in the municipality of Chisinau.

2. Materials and Methods

It was analyzed the results of laboratory investigations of samples of different vegetal food – stuffs, especially vegetables made in the Center of Preventive Medicine of municipality of Chisinau, Republic of Moldova during the last

5 years period (2003–2007). The laboratory investigations were made by approved potentiometric method.

3. Results

There were analyzed in all 3,451 samples of vegetal food – stuffs, mainly vegetables. Every year the number of samples was different. So, if in the first year of the study there were analyzed only 461 samples, but in the next year the number of samples was significantly raised – up to 863. In years 2005, 2006 and 2007 there were analyzed 679, 854 and 594, respectively. The parts of concrete food – stuffs in general structure were different too. On the first three places there were samples of potatoes, cabbages and carrots with the part between 16.7–9.7%, followed by the samples of tomatoes, beet-roots and onion (8.0–6.7%). The parts of other vegetables were under 5% for every of them. Total part of the samples of fruits, grapes, mushrooms and berries were 5.7–8.2%. The results of laboratory investigations were compared with official norms in the Republic of Moldova and were processed statistically.

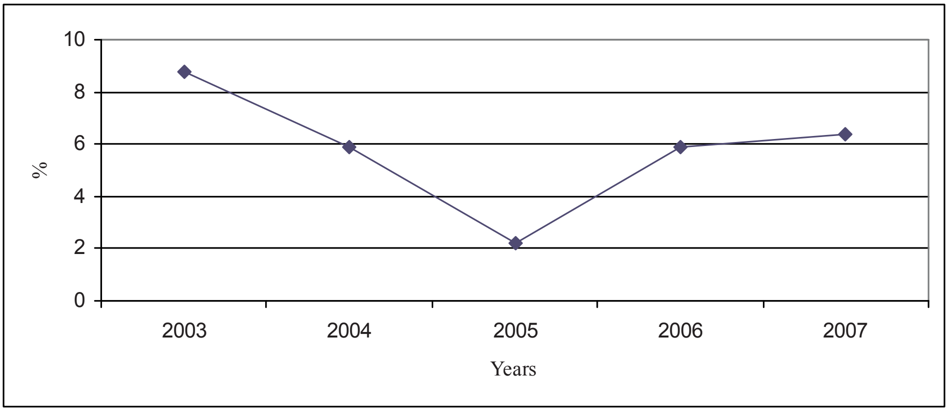

Figure 1. The general average parts of food-staffs' samples with increased quantities of nitrates.

In general, every year during the period of study it was established the lowering of parts of samples with increased quantities of nitrates. The highest part of food-stuffs' samples with increased quantities of nitrates (over norms) were revealed at the beginning of the study in 2003 and the lowest-in the middle of this period, in the year 2005. So, the average part of these samples were 8.8%; 5.9%; 2.2%; 5.9% and 6.4% in the years 2003, 2004, 2005, 2006 and 2007, respectively (Figure 1).

In year 2005 the nitrates over norms were revealed only in a few kinds of vegetables (beet roots, potatoes, radish, autumn cabbage, melons). Quantities of nitrates over norms never were revealed during the period of study in fruits, grapes, mushrooms and different berries. On the other hand every year were established nitrates over norms in samples of radish, beet – roots, potatoes and autumn cabbage (Figure 2).

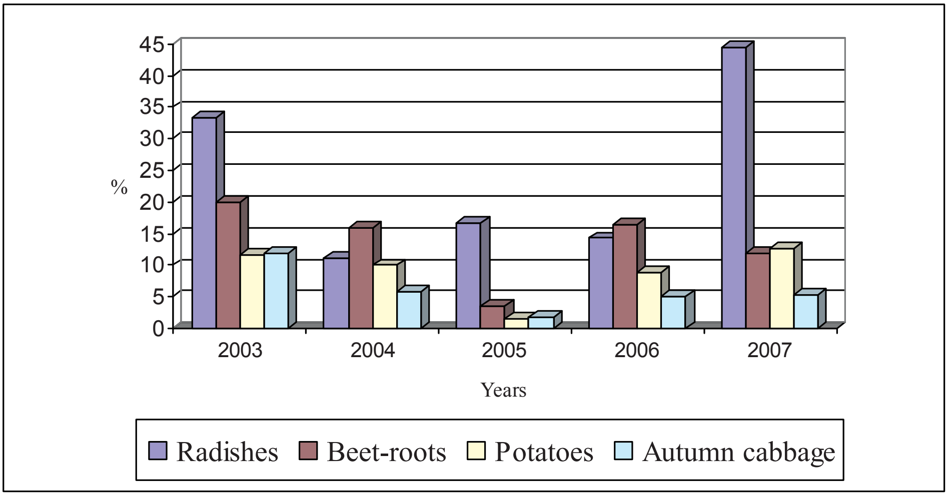

Figure 2. The average parts of food-staffs with increased quantity of nitrates every year during the study.

The average part of samples with contents of nitrates over norms were 23.9%; 13.6%; 8.9% and 6.0% for every kind of vegetables, respectively. The increased quantities of nitrates in radish were revealed in the first and in the last years of the study, the parts of these samples having been 33.3% and 44.4% respectively, while in years 2004, 2005 and 2006 the parts of samples with nitrates over the norms were 11.1%; 16.7% and 14.3%. The part of beet-roots' samples with increased quantities of nitrates during the first 3 years took down especially in the year 2005 (20.0%; 15.9%; 3.6%), but raised in 2006 (16.5%) and then decreased again in the last year of the study (11.8%). The lowest part of samples with increased quantities of nitrates were established in year 2005 (1.8%), while in other years the parts of these samples were higher and nearly at the same level (11.6%; 10.0%; 8.9%; and 12.6% in years 2003, 2004, 2006 and 2007). Similarly the samples of beet – root the samples of potatoes with increased quantities of nitrates also decreased in the first 3 years of the study (12.0%; 5.8%; 1.8%), but then raised and settled down and were practically at the same level (5.0% and 5.4%) in 2006 and 2007, respectively.

There were established increased quantities of nitrates during 4 years from those 5 years of this study in vegetable marrows and melons (Figure 3).

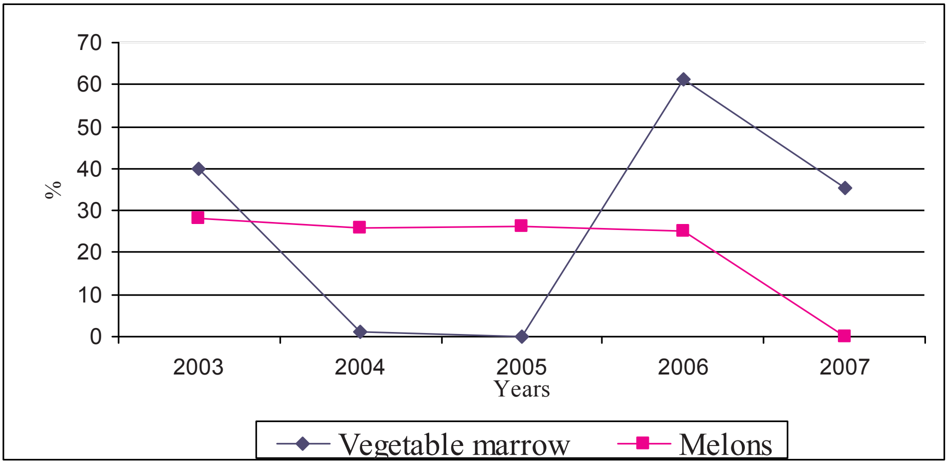

Figure 3. The average parts of samples of vegetables marrow and melons with increased quantities of nitrates.

The contents of nitrates were in limits of norms in samples of vegetable marrows in 2005 and in samples of melons – in the last year of the study. It must be mentioned, however, that the average part of vegetable marrow's samples with increased quantities of nitrates for all 5 years was the highest in comparison with other investigated samples of food – stuffs of vegetal origin (27.5%). The highest part of vegetable marrows' samples with increased quantities of nitrates was established in the year 2006 (61.1%) and the lowest – in the year 2004 (1.2%), while during the first and the last years the parts of samples with increased quantities of nitrates were 40.0% and 35.3%, respectively. The average part of melons' samples with increased quantities of nitrates for all period was 21.1%, having been every year at the same level (28.0%; 25.9%; 26.3% and 25.0% in the years 2003, 2004, 2005 and 2006, respectively).

There were increased quantities of nitrates in samples of carrots during 3 years, in samples of green onions and green grocery – in 2 years. So, the parts of carrots' samples with raised quantities of nitrates were revealed in the years 2003, 2004 and 2006 with the average of 4.3%; 5.9% and 2.2%, respectively. The green onions' samples with raised quantities of nitrates were revealed in the years 2004 and 2007 with average parts 33.3% and 16.7% and the green grocery's samples with increased quantities of nitrates were established in the years 2006 and 2007 (5.9% and 4.5%, respectively). Increased quantities of nitrates in samples of summer cabbage, water – melons, onions, cucumbers and eggplants were established only in 1 year during 5 years' period of the study. So, in the first year of this study were established increased quantities of nitrates in samples of summer cabbage and water-melons, in the second – in samples of onions and cucumbers and, finally, in 2006 nitrates in increased quantities were established in samples of eggplant with average parts 11.2%; 9.8%; 5.0%; 4.1%; and 6.7%, respectively.

4. Discussion

The obtained data show that some vegetables can accumulate nitrates in increased quantities. It is important to mention this fact because many literature references indicate the unfavorable influence of nitrates upon mammals in experiments. From this point of view it is interesting to note, that every year in some vegetables (beet – roots, potatoes, radish, autumn cabbage) there were established increased quantities of nitrates. During 4 years the quantities of nitrates had exceeded norms in different parts of samples of vegetable marrow and melons, 3 years – in samples of carrots, in samples of green onions and green grocery – during 2 years and only in 1 year – in samples of summer cabbage, water – melons, onions, cucumbers and eggplants. In ten kinds of vegetables raised quantities of nitrates were established during the second year of study, in nine kinds – in the first and in the last but 1 years, in seven – in the last year and only in five kinds – in the middle year of this study. Usually the quantities of nitrates exceeded the norms with 20–40%. On the other hand quantities of nitrates over the norm were never revealed during the period of study in fruits, grapes, mushrooms and different berries. In general, in comparison with the results of the same laboratory investigations of different food – stuffs obtained 25–30 years ago (Opopol and Dobrianskaya, 1986) during the period of this study the situation was better. May be this fact is explained by the use of a smaller quantities of fertilizers by farmers and liquidation of great stock – breeding farms.

Recently (2008) it was established a favorable influence of a small quantities of nitrates upon different organs and systems of human organism. So the Swedish researcher Joel Petersson from Uppsala University's Department of Medical Cell considers that nitrate-rich vegetables such as spinach, lettuce, radishes and beetroot have a positive influence on the stomach by activating the mucous membranes' own protective mechanisms, thus reducing the risk of problems such as gastric ulcers (http://www.newsmax.com). It is considered also that nitrates from different vegetables like spinach and lettuce may keep blood vessels healthy and lower blood pressure (http://www.newsmax.com). However the fact of accumulation of nitrates in quantities over the norms in some food – stuffs of vegetal origin, especially, vegetables confirm the necessity of permanent hygienic supervision. This necessity will be more important in the future when the farmers will be able to buy more quantities of fertilizers than now.

5. Conclusions and Recommendations

- There were established the contents of nitrates over the norms, especially, in vegetables.
- Contents of nitrates over the norms never were revealed during the period of study in fruits, grapes, mushrooms and different berries.
- The hygienic supervision upon the contents of nitrates remains necessary for the future.
- Based on the results of laboratory investigations can be proposed a modification of scheme of food – stuffs’ samples selection.
- If nitrate levels in vegetables are too high, growers must reduce the amount of nitrogen fertilizer they apply.

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CHLOROSIS RISK EVALUATION FROM A NEW VITICULTURE AREA LOCATED ON A FORMER ARMY REGION

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Abstract. In this work are presented original studies regarding soil characterization from a former army area, located in Nazarcea, Constantza, in order to setting out new viticulture area and to evaluate the chlorosis risk. Sodium chloride, total iron, potassium, calcium carbonate, phosphates and humus have been analyzed in soil samples by titrimetric and spectrometric methods. Physical characteristics such as pH and granulometry have been also determined. The mean of chlorotic power index (CPI), calculated for all analyzed samples show high values: 11.76 (0–20 cm depth), 73.48 (20–50 cm depth) and 108.66 (50–110 cm depth) that means high risk of chlorosis.

Keywords: chlorosis risk, iron, active calcium carbonate, chlorotic power index

1. Introduction

Environmental soil chemistry knowledge is paramount to predicting the fate, mobility and potential toxicity of contaminants in the environment. Understanding the adsorption/desorption, precipitation, polymerization, dissolution, complexation, and oxidation/reduction processes will enable to better predict the fate and toxicity of contaminants and will ultimately provide the knowledge to develop sound and cost-effective remediation strategies (Sparks, 2003).

Soil is the most valuable and non-renewable resource. It is the basic medium of life support for human beings, animals, flora, fauna and many other organisms.

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Soil characterization data are a key piece of the picture of how an ecosystem works. The determination of the properties of soil horizons can predict how fast water will move through them. Soil properties also show whether the soil has the potential to store enough water to keep plants growing through a drought, to withstand a flood, and to provide the right combinations of chemicals to plants (as indicated in measurements of pH, and Fe, P, $CaCO_3$, K levels) so that they will grow properly. The chemical and physical properties of soils represent specific information about how well the soil will perform as a filter of wastes, as a home to organisms, as a location for buildings, and in other important uses. The more information exists about soil properties, the more it can be evaluating the quality of natural resources all over the world.

Once a site is suspected of being contaminated there is a need to assess the contamination. The historical use of the site and the materials used and produced on site will guide the assessment strategy and type of sampling and chemical analysis to be done. Often nearby sites owned by the same company or which are nearby and have been reclaimed, levelled or filled are also contaminated even where the current land use seems innocuous (Pestana et al., 2005).

For example, a car park may have been levelled by using contaminated waste in the fill. Also it is important to consider off site contamination of nearby sites often through decades of emissions to soil, groundwater, and air.

Iron, though in small amounts, is one of the minerals required by plants for a healthy growth. This mineral element is utilized by plants in the following forms: as ferrous Fe(II) or ferric Fe(III) ions, hydrated or complexed by other ligands.

In plants iron is found bound mainly to various amino acids that form part of the plant proteins; it binds also to some other polymers. Iron is involved in the enzyme systems. For example, it actively participates in redox reactions of photosynthesis, respiration, biosynthesis of proteins and chlorophyll, biological binding of atmospheric nitrogen, and in the reduction of nitrates and nitrites (Tagliavini and Rombola, 2001).

Deficiency of iron in plants, especially in fruit trees, including grapes and roses, results in chlorosis. The mentioned agricultural crops are characteristic for the area of study. Iron deficiency is also called lime-induced chlorosis. As the soil pH rises over 7, or in heavily limed soils, iron becomes unavailable to plants (Tagliavini et al., 1993). Occasionally, a few plants may exhibit iron-deficiency symptoms. These are often located near the site of previous lime or building plaster storage where the soil pH is abnormally high. Iron deficiency may also occur in isolated parts of the field or on a few individual plants. Iron deficiency causes interveinal chlorosis of new leaves. As the condition becomes more severe, the whole leaf becomes pale yellow. Quite often only one side or one branch of the plant is affected. Initial symptoms of iron deficiency are a yellowing or chlorosis between the veins of younger leaves (Himelick and Watson, 1990). The veins usually remain green. In more severe cases, interveinal and marginal browning or necrosis occurs. This is followed by premature leaf drop and dieback of twigs and branches. Fungal leaf spots are more common on leaves with iron deficiency and may tend to make the necrosis appear worse. The purpose of the paper is to present the studies performed to set up new viticulture areas on a former military area, located in Poarta Alba – Nazarcea Constantza.

2. Experimental

In order to realize the proposed objective, the soil was physico-chemical characterized and the chlorosis risk was calculated. Five longitudinal sections of soil samples (profiles 1–5) have been collected from the studied area in April 2008 at depths of 0–20 cm, 20–50 cm and 50–110 cm.

The granulometry analysis was done by Kacinsky method. pH and salinity were determined by electrometric method with pH Cond707 apparatus.

Active calcium carbonate, total calcium carbonate and total iron concentration were determined by titrimetric and spectrometric methods described before (Nicolaescu et al., 2007). Phosphorus concentration was determined in the solution obtained by extraction from soil samples with ammonium acetate lactate (AAL) solution at pH 3.75. The phosphate anion was determined as “molybdenum blue”. The spectrometric measurements were done with Cintra 404 UV-Vis apparatus.

The potassium concentration was measured with flame photometer 425 Sherwood (air/methane) in the solution obtained by extraction with AAL at pH 3.6–3.7 (adjusted using HCl solution). The ratio soil sample: extracting solution was 1:50.

The chlorotic power index (CPI) was calculated with the C. Juste and P. Pouget formula:

$$CPI = \frac{active\ \ CaCO_3,\%}{(Fe, ppm)^2} \times 10^4$$

Soil chlorosis evaluation can be characterized using the Table 1 where the chlorosis intensity degrees for CPI values are presented (Rusu et al., 2005).

TABLE 1. The chlorosis intensity degrees for different CPI values.

CPI values	Chlorosis intensity
0	That’s not the case
≤5	Small
6–15	Medium
16–35	High
≥36	Very high

3. Results and Discussions

The obtained granulometry data show that soils texture are medium for all depths (0–50 cm depth clayey; >50 cm depth sandy-clay) (Figure 1).

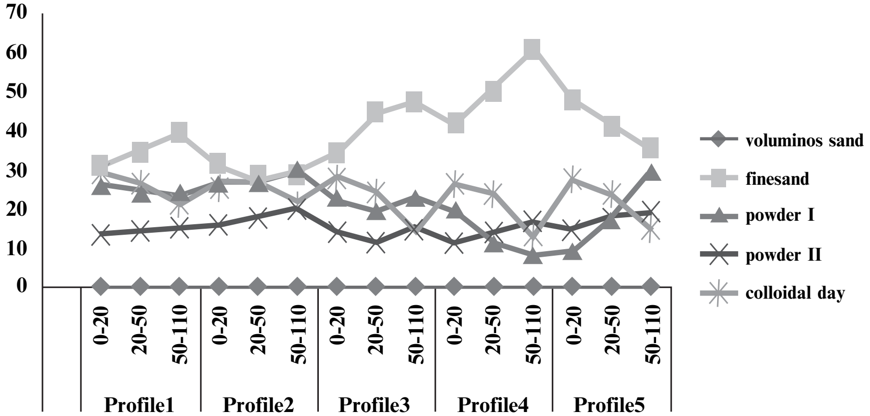

Figure 1. Soils granulometry analysis for all analyzed profiles (%).

The pH (Figure 2) and salinity (Figure 3) results show that the soil has low alkaline and a very low salinity.

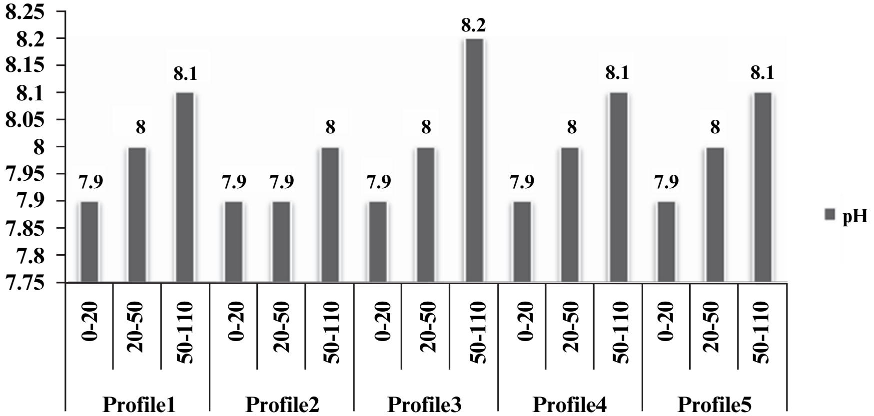

Figure 2. pH characterization for all analyzed profiles of soil in Poarta Alba – Nazarcea Constantza.

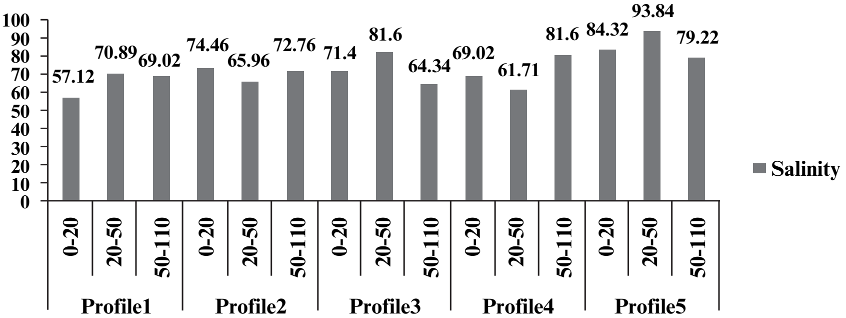

Figure 3. Salinity determination for all analyzed profiles of soil in Poarta Alba – Nazarcea Constantza (mg/100 g soil).

The phosphorus, potassium and iron determinations in the soil profiles samples showed that plant available phosphorus concentration between 0–20 cm depths is high and it's decreasing between 21–100 depth, plant available potassium concentration is very high for all depths and Fe concentration is medium between 0–20 cm depths and very low between 20–100 cm depth (Figure 4).

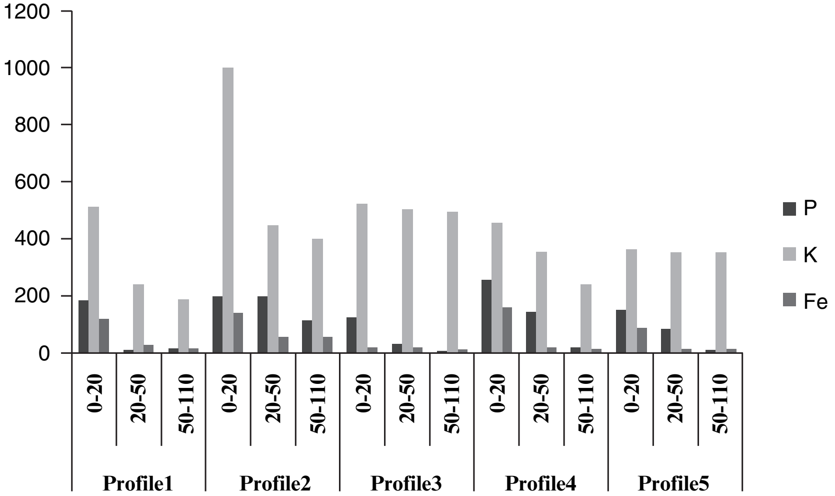

Figure 4. P, K and Fe concentrations in analyzed soil for all profiles (ppm).

The results for humus, total calcium carbonate and active calcium carbonate for the analyzed soil samples are presented in the Figure 5.

The data relived that humus content between 0–50 cm depths is very high and it's decreasing between 50–100 depths; total $CaCO_3$ content between 0–50 cm depths is medium and increases to very high level after 50 cm depth and active $CaCO_3$ content is medium between 0–20 cm depths and have increasing shape to high level after 21 cm depth.

The calculated CPI for all analysed profiles (Figure 6) is predominant higher than 36 in soils collected from 20–100 cm depth.

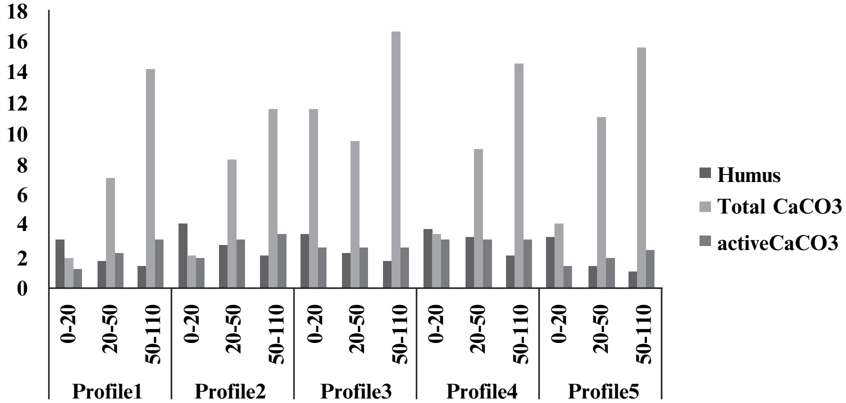

Figure 5. Humus, total calcium carbonate and active calcium carbonate concentration of in analyzed soil for all profiles.

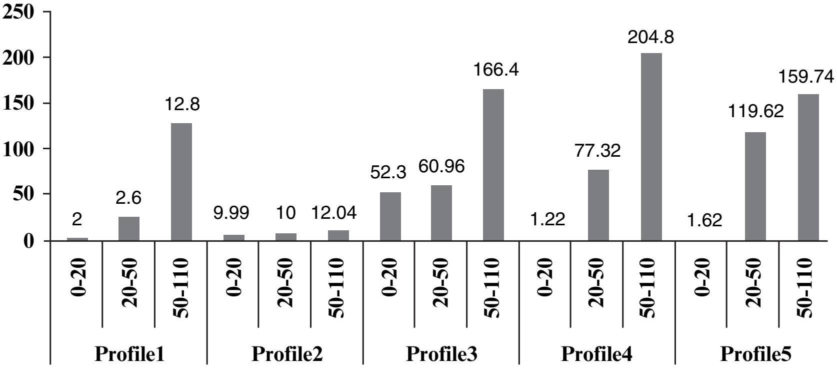

Figure 6. Chlorothic power index (CPI) for all depths in the analyzed soil samples.

The high and very high values of chlorotic power indexes for the studied soils require a special monitoring of resistant layers at iron chlorosis (Ocete et al., 2008; Pestana et al., 2005; Yeh et al., 2000).

4. Conclusions

The investigations carried out for setting up new viticulture area Nazarcea, Constanta on a land which belong to a military unity showed that soils have medium and high active $CaCO_3$ content, a low alkaline pH and a low and very low soluble iron content. Because the values of chlorotic power indexes which are very low between 0–20 cm depth, high between 20–50 cm depth and extremely high between 50–100 cm the risk of iron chlorosis for this soil is very high. In order to carry out for setting up new viticulture area there are required a special monitoring of resistant layers at iron chlorosis as well as the necessity of iron mineral nutrients adding on the vegetation period.

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PESTICIDE RESIDUES DETERMINATION IN VEGETABLES FROM ROMANIA BY GC-ECD

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Abstract. Pesticide use raises a number of environmental concerns. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments and food. Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. In this study the organochlorine pesticides have been measured in vegetables samples from Dobrogea county, Romania, by gas chromatography with electron capture detector (GC-ECD) after extraction and clean-up step and also the calculated bioconcentration factor (BCFs values) were used to relate pesticide residues in plants to the pollutant concentration in soils. The pesticides concentrations were at ppb levels and BCFs values were below 1.

Keywords: OCPs, vegetables, GC-ECD, BCFs values

1. Introduction

Human beings are now exposed to widespread chemical/toxic pollution caused by multiple substances or chemicals that affects human health. The toxic effects are often due to a poorly regulated marketing of chemicals, but also to inadequately controlled management and monitoring of production, consumer use and disposal of the chemicals. Most of the substances or products are currently being marketed without prior and sufficient toxicological testing and

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risk assessment for human health. The numerous chemical substances or products cause a widespread dispersed contamination throughout the environment; whereas they interact with one another causing additional and/or synergic toxic effects in the environment and/or living organisms. It is therefore extremely difficult to produce evidence at the epidemiological level of a direct link between exposure to one and/or other of the chemical substances or products and the development of specific diseases. These substances or chemicals are more and more numerous: polyaromatic hydrocarbons (PAHs), organo-halogenated derivatives, toxic metals, pesticides, food additives and others. Some of them are persistent in the environment and contaminate the air, water, soil and food, so people are constantly exposed to persistent toxic substances or products, including Persistent Organic Pollutants (POPs). Pesticides are widely used in fruit and vegetables cultivation because of their susceptibility to insect and disease attacks. Therefore, residues of pesticide could affect the ultimate consumers especially when vegetables and fruits are freshly consumed. The risk posed by contaminated food must be identified, accessed, and remediated.

The Stockholm Convention on Persistent Organic Pollutants was adopted in May 2001 with the objective of protecting human health and the environment from the potential risks of persistent organic pollutants. Romania has ratified Stockholm Convention by the Law no 261 of June 2004 and becomes a Party of the Convention on 28 October 2004. As a part of the convention, Romania elaborated National Implementation Plans, document which has been send to the Stockholm Convention Secretariat on April 2006. The overall objective of the National Implementation Plans is to reduce or eliminate releases from the existing stockpiles and wastes; to eliminate production of POPs; to restrict the use of DDT and to reduce unintentionally releases of Dioxins, HCB and PCBs from the social and economic activities (Betianu and Gavrilescu, 2006).

In 1948 organochlorine pesticides have been used for the first time in Romania. The first products were based in principal on DDT but it had been also used other products based on endrin, dieldrin, aldrin, heptachlor, chlordane and toxafen. Since 1988 these kinds of products are banned or restricted in Romania and in the present only chlorinated insecticides on the base of lindane are used for seeds treatment; lindane is not included in the Stockholm Convention list (Condurateanu and Cadariu, 2006).

The risk from pesticide residues is evaluated on the basis of two toxicological limit values: the Acceptable Daily Intake (ADI) and the Acute Reference Dose (ARfD).

The ADI indicates the amount of a substance which can be ingested daily over a lifetime by consumers without any appreciable health risk and is used to assess the chronic risk whereas the ARfD to assess the acute risk. The ARfD is a comparatively new risk assessment tool. It is defined as the amount of a substance which a consumer can ingest from one meal or several meals spread over the day without any appreciable health risk. A one-off exceeding of the ADI value is not relevant as this value takes into account the lifelong daily intake of a substance. Even a short-term exceeding of the ADI value does not constitute a risk for consumers. By contrast, a possible health impairment of the consumer cannot be ruled out from the very outset in conjunction with a one-off or short-term exceeding of the ARfD. It must be examined in each individual case whether damage to health is, in fact, possible.

In principle, if the maximum permissible level for pesticides is complied with, then the ARfD will not be exceeded. There are two possible considerations which could lead to a temporary deviation from this rule:

1. A maximum residue level was derived when the assessment of risks from the short-term intake of a substance was not yet used as the basis for assessment. If the maximum level proves to be too high in conjunction with later consideration of the ARfD, then the maximum level will have to be adjusted to bring it into line with existing statutory provisions and ordinances.
2. New scientific findings are available which require a review of the existing toxicological limit values and may justify a raising or lowering of the ARfD. In this case it may be necessary to adjust the maximum levels too (Federal Institute for Risk Assessment, 2008).

Most analytical methods in the literature involve extraction of pesticide residues from food by organic solvents, surfactants, supercritical fluids or solid-phase extraction followed by GC, HPLC, GC-MS or ICP determination (Pihlström et al., 2007; Mol et al., 2007; Lambropoulou and Albanis, 2007; Pozo et al., 2007).

The aim of this study was to determinate the levels of organochlorine pesticides from seven species of vegetables collected from urban and rural sites belonging to Dobrogea county, Romania, using GC-ECD.

2. Experimental

2.1. SAMPLING

Seven species of vegetables have been collected from different sites in Dobrogea County, Romania: parsley and dill from rural area Slava Rusă and from urban area Constantza, carrot and celery from rural area Greci and from urban area Medgidia, cucumber from rural area Adamclisi and from urban area Tulcea, onion and garlic from rural area – Ciobanu. Different parts of vegetables have been analysed: steam and leaves (parsley and dill), bulb and leaves (celery, carrot, onion and garlic) or fruits (cucumber).

2.2. REAGENTS AND SOLUTIONS

Standards of pesticides: HCB, Lindane, p,p'-DDT, p,p'-DDE, p,p'-DDD, Aldrin, Dieldrin, Endrin, Heptachlor were supplied by International Atomic Energy Agency, Monaco laboratory.

Florisil was assayed for preconcentration step as sorbent material of variable polarities. It (60–100 mesh) was obtained from Fluka (packed in Switzerland) and was activated overnight (12 h) at 130°C before use. Anhydrous sodium sulphate (granulated for residue analysis – Merck) was activated at 200°C for 2 h before use. As eluents two organic solvents there were used: n-hexane, supplied by Merck, Darmstadt, Germany and dichloromethane supplied by J.T. Baker.

2.3. SAMPLE EXTRACTION

All of vegetables samples were handled by Soxhlet extraction and an aliquot of the extract was applied to 5 g of activated florisil column for pesticides, topped with 1 cm of anhydrous sodium sulfate, which was pre-washed with n-hexane as described in EPA methods 8270C and 3600C. The columns were eluted with n-hexane-dichloromethane (3:1). Each fraction was concentrated to 1 mL using the Kuderna–Danish concentrator. The concentrated aliquot was blown down with nitrogen, the internal standards (2,4,5 trichlorobiphenyl) were added, and the final volume was injected. A Hewlett-Packard 5890 gas chromatograph (GC) equipped with an electron capture detector (ECD) has been used for determinations. The GC was equipped with a HP–5 fused–silica capillary column (30 m × 0.32 mm × 0.25 μm), helium was used as the carrier gas with flow rate 1.36 mL/min and nitrogen makes-up gas at 40 psi. The injector and detector temperatures were 250°C and 300°C, respectively. The initial temperature was 60°C, after 1 min the temperature was increased to 300°C at a ramp rate of 20°C/min and then held for 10 min.

2.4. INSTRUMENTAL ANALYSIS

Table 1 shows the quality parameters of the method and the maximum residue levels of pesticides in vegetables adopted by European Commission (Commission regulation (EC) 149/2008). Detection limits (LOD) were calculated from spiked field blank chromatograms at the lowest concentration giving a response of three times the average of the baseline noise (three injections).

TABLE 1. Quality parameters of the method.

Pesticides	Retention time (min)	LOD (ppb)	Maximum residue levels (mg/kg) European Commission
Lindane	11.15	0.3	0.01
p,p’-DDT	16.98	0.2	ΣDDT-0.05
p,p’-DDE	15.44	0.2	
p,p’-DDD	16.22	0.2	
HCB	10.53	0.3	0.01
Aldrin	13.42	0.2	0.01
Dieldrin	15.78	0.2	0.01
Endrin	15.97	0.3	0.01
Heptachlor	11.35	0.2	0.01

3. Results and Discussions

The levels of organochlorine pesticide residues found in vegetables samples are given in Tables 2, 3 and 4. Examination of the data show that some residues of the studied pesticides were below the quantification limits. In the majority of the samples the detected pesticides varies at different levels.

Data on vegetables samples collected showed that the higher pesticide’s concentration was found in parsley’s stem (2.276 ppb) grown in urban area. DDD, DDE, DDT and dieldrin concentrations were under the quantification limit.

The results of this study may be compared with those of monitoring programs like the French program (Ministère de l’économie des finances et de l’industrie, 2004) were dieldrin and lindane were detected in 0.1% of vegetables while in the United Kingdom program (Pesticide Residues Committee, 2006) only 0.5% of vegetables had dieldrin and no residues were found in cereals and fruits.

Based on the obtained results, it can be stated that the values are situated within the limits imposed by the last regulations of European Commission. The bioconcentration factors (BCFs values) were calculated for a generally applicable exposure assessment of the correlation between the concentrations in the soil and the concentrations in vegetables. BCFs values were calculated as the ratio between the concentrations in plants and soil. The BCFs values were below 1 and these values were decreased with increasing concentrations in soil.

TABLE 2. Pesticide concentrations in parsley and dill (ppb).

Pesticides (ppb)	Parsley Urban area Constantza		Parsley Rural area Slava Rusă		Dill Urban area Constantza		Dill Rural area Slava Rusă	
	Stem	Leaves	Stem	Leaves	Stem	Leaves	Stem	Leaves
Lindane	2.276	0.703	0.534	0.662	0.356	0.320	<LOQ	0.315
HCB	0.327	<LOQ	<LOQ	<LOQ	0.588	<LOQ	<LOQ	<LOQ
Hepta chlor	0.252	<LOQ	<LOQ	<LOQ	0.224	<LOQ	0.315	0.445
Aldrin	0.330	0.308	<LOQ	<LOQ	1.728	0.549	0.684	0.308
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	0.480	0.346	0.469	0.369	0.346	<LOQ	<LOQ	<LOQ
DDD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DDE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DDT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

*LOQ – quantification limit.

TABLE 3. Pesticide concentrations in vegetables (ppb).

Pesticides (ppb)	Celery Urban area Medgidia		Celery Rural area Greci		Carrot Urban area Medgidia		Carrot Rural area Greci	
	Bulb	Leaves	Bulb	Leaves	Bulb	Leaves	Bulb	Leaves
Lindane	<LOQ	1.102	<LOQ	0.433	0.446	0.340	0.356	0.407
HCB	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hepta chlor	<LOQ	0.329	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Aldrin	<LOQ	1.212	<LOQ	0.605	0.819	0.211	0.258	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	0.397	<LOQ	0.482	0.426	<LOQ	0.564	<LOQ
DDD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DDE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DDT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

*LOQ – quantification limit.

TABLE 4. Pesticide concentrations in vegetables (ppb).

Pesticides (ppb)	Cucumber Urban area Tulcea	Cucumber Rural area Adamclisi	Garlic Rural area Ciobanu		Onion Rural area Ciobanu	
	Fruit	Fruit	Bulb	Leaves	Bulb	Leaves
Lindane	<LOQ	<LOQ	<LOQ	<LOQ	0.396	0.363
HCB	<LOQ	<LOQ	0.323	<LOQ	<LOQ	<LOQ
Heptachlor	<LOQ	<LOQ	0.312	<LOQ	0.235	<LOQ
Aldrin	0.230	0.347	0.230	<LOQ	0.457	0.250
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	0.348	<LOQ	<LOQ	<LOQ
DDD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DDE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DDT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

*LOQ – quantification limit.

4. Conclusion

The paper presents original studies concerning the organochlorine pesticide residues determination in vegetables from Romania in order to ensure safety and quality. The pesticides concentrations were at ppb levels and BCFs values were below 1.

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HEAVY METALS AND PESTICIDES ANALYSIS FROM BLACK SEA ALGAE

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Abstract. Our studies were focused on heavy metals (Cd, Cu, Zn, and Pb) and pesticides analysis from two different types of marine algae in order to assess their capabilities to be used as raw material for pharmaceutical purposes without risks for human health. The analysed algae, *Cystoseira barbata* and *Ceramium rubrum,* have been collected from Romanian Black Sea Coast in the southern zone Tuzla – Vama Veche where the biomass has increased in 2007. The used analytical techniques were atomic absorption spectrometry (AAS) for heavy metals and gas chromatography with electron capture detector (GC-ECD) and thermoionic specific detector (GC-TSD) for organochlorine respectively organophosphoric pesticides. The results indicate that heavy metals and pesticides levels are very low, similar with other reported data. The bioaccumulation abilities for studied contaminants are higher for *Ceramium rubrum* than for *Cystoseira barbata*.

Keywords: heavy metals, pesticides, marine algae, AAS, GC-ECD, bioconcentration

1. Introduction

During the past few decades, the Black Sea has been subjected to various human impacts that have led to changes in the ecology of this inland sea. River runoff has introduced high levels of certain heavy metals and other toxic substances. Ship traffic has led to the introduction of new species, and fishing

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pressures have also altered the ecology of the area. The underlying principles of the Convention on Protection of the Black Sea against Pollution (1992) imply a holistic approach to monitoring and assessment of the Black Sea ecosystem.

One of the difficulties in forming balanced judgments of the impacts of marine pollution on human and other species is that human and ecological risk assessments are usually conducted separately. Although both human and ecological risk assessment protocols have a common goal, "to provide a quantitative estimate of the probability of one adverse effect occurring as a consequence of a contaminant release" (Newman, 1998) there are differences in regulatory practice, emphasis and technical feasibility that lead to differences in the endpoints commonly considered (Sutter et al., 2004). Human health risk assessment is focused solely in the protection of human health and considers the effects on the individuals, whereas ecological risk assessment also considers the consequences for populations, communities and ecosystems giving less emphasis to the impact at the individual level. It is critical to evaluate the bioconcentration of toxic chemicals in relation to human consumption and public health effects (CIESM, 2007).

Heavy metals such as lead, cadmium, mercury and arsenic, occurring in soil, water and food affect health considerably both in human and in animals. (Duchiron et al., 2002).

Organochlorine pesticides (OCPs) are known to be exclusively anthropogenic organic persistent pollutants. They have been worldwide contaminants in 1969, but nowadays their use has been prohibited in most countries. OCPs can be carcinogenic, citogenic and can produce bone marrow diseases, infertility, nerve disorders and immunological and respiratory diseases (Albareda-Sirvent et al., 2001).

Accumulation of heavy metals and pesticides in marine environment has been extensively studied using marine macroalgae due to their ability to concentrate and tolerate high metal levels. Macroalgae have been shown to be good bioindicators of heavy metal and organic pollutants contamination in seawater and also being one of the primary producers of the food chain generally can provide one of the first signals for the living status of marine ecosystems. (Al-Homaidan, 2006).

Cystoseira barbata is a brown algae growing spontaneous in coastal areas in the Black Sea (0.5–10 m) where the sunlight is entering and some quantities of the metals present in water are transferred through the biogeochemical chain of photosynthesis process.

Ceramium rubrum is a red algae which lives at greater depths, where the sunlight is absent, photosynthesis cannot be achieved and where heavy metals sediments are depositing because of the specific Black Sea's marine currents.

The aim of the work is to report new results concerning heavy metals (Cd, Cu, Zn, and Pb) and pesticides analysis from two different types of marine algae (*Cystoseira barbata* and *Ceramium rubrum*) in order to assess their capabilities to be used as raw material for pharmaceutical purposes without risks for human health. In the same time the bioconcentration factors for the studied contaminants have been calculated.

2. Experimental

Marine algae samples (*Cystoseira barbata* and *Ceramium rubrum*) were collected on the Romanian Black Sea Coast, Tuzla – Vama Veche area where the biomass has increased during the summer of 2007.

For heavy metals analyses, the marine algae samples were carefully selected, washed and dried 16 h at 105°C and mineralized by dry ashing method using MLW112 ashing furnace. About 10 g of each dried marine algae sample were weighed into porcelain crucibles, treated with 3 mL $Mg(NO_3)_2$ solutions and heated in the programmable furnace. The heating process was performed by increasing the temperature 2 h at 250°C, 3 h at 350°C and 3 h at 450°C when a white ash resulted. After cooling, the samples were treated with 5 mL HCl (1:1) solution then with 1 mL CH_3COOH and evaporated on a water bath until a residue was formed.

The residue was dissolved in 5 mL deionised water and make up to 100 mL with H_2O. All used reagents were of analytical reagent grade (Merck). The resultant solutions were analyzed with atomic absorption spectrometer GBC-Avanta (air/acetylene flame) for the determination of heavy metals concentration: Cd (λ = 228.8 nm), Cu (λ = 324.7 nm), Zn (λ = 213.9 nm) and Pb (λ = 270 nm). Three replicate determinations were done for each solution.

Organochlorine pesticide residues were extracted from samples with n-hexane in a Soxhlet apparatus and then were purified on fluorisil column with a layer of anhydrous Na_2SO_4.

Organophosphoric pesticide residues were extracted from samples with n-hexane for 15 min in an ultrasonic bath Sonica 3200 EP, and then were purified on fluorisil column with a layer of anhydrous Na_2SO_4.

In order to purify the obtained extracts, a total of 10 g fluorisil was packed in a glass column with n-hexane. 20 mL fractions of each extract of pesticides were eluted from the column with a mixture of ether petroleum and ethyl ether (94:6 v/v for organochlorine pesticides and three different ratios 94:6; 85:15 and 50:50 v/v for organophosphoric pesticides). The both pesticide residues fractions were concentrated to about 5 mL with Buchi rotary evaporator at 30–35°C on vacuum.

For analysis Varian gas chromatograph equipped with capillary column and electron capture detector (GC-ECD) and thermoionic specific detector (GC-TSD) for organochlorine respectively organophosphoric pesticides was used. The applied conditions were: volume of injected extract – 1 μL; column temperature 200°C; injector temperature 210°C; detector temperature 250°C; carrier gas: nitrogen at a flow rate of 4 mL/min.

3. Results and Discussions

In Figure 1 the mean concentration values of Cd, Cu, Zn, and Pb in the analyzed marine algae (*Cystoseira barbata* and *Ceramium rubrum*) are presented. For all determined heavy metals, the measured concentrations are similar with results reported by other researchers in Black Sea (Kut et al., 2000; Topcuoglu et al., 2003) or Aegean Sea (Savidis et al., 2001). In *Ceramium rubrum* Cd, Cu, Zn and Pb concentrations are bigger than in *Cystoseira barbata.* This fact can be explained by their habitat on the sea level or by the specific metabolism of each alga.

In order to have a comparative study between our original data and other researchers' data (Chirila et al., 2005; Petisleam et al., 2005, 2006) concerning the metal concentrations in both studied algae from Black seacoast over the last 5 years, Figure 2 presents the monitoring data from 2003 until 2007. Copper concentrations in the last 5 years have a decreasing shape in brown algae *Cystoseira barbata*, while increasing in the red algae *Ceramium rubrum*. Cd, Zn and Pb concentrations in the last 5 years have not significant changes.

The analysed organochlorine pesticides were: hexachlorocyclohexane (α-HCH; β-HCH, γ-HCH, δ-HCH), aldrin, heptaclor, dieldrin and endrin. The founded concentrations in the analyzed marine algae samples are presented in Table 1.

Organochlorine pesticide analysis showed the presence of γ-HCH in *Cystoseira barbata*, lower than the γ-HCH concentration in *Cernamium rubrum* where δ-HCH has been also found.

The organophosphoric pesticides in the analyzed samples were not detected. The studied pesticides which have been checked having available standards were: phorate (*o,o*-diethyl *S*-ethylthiomethyl phosphorodithioate) (9.998 min), disulfoton (*o,o*-diethyl *S*-2-ethylthioethyl phosphorodithioate) (10.811 min), methyl parathion (11.152 min), runnel (11.573 min), malathion (11.857 min), parathion (12.015 min) and ethion (*o,o,o′,o′*-tetraethyl *S,S′*-methylene bis (phosphorodithioate) (13.753 min).

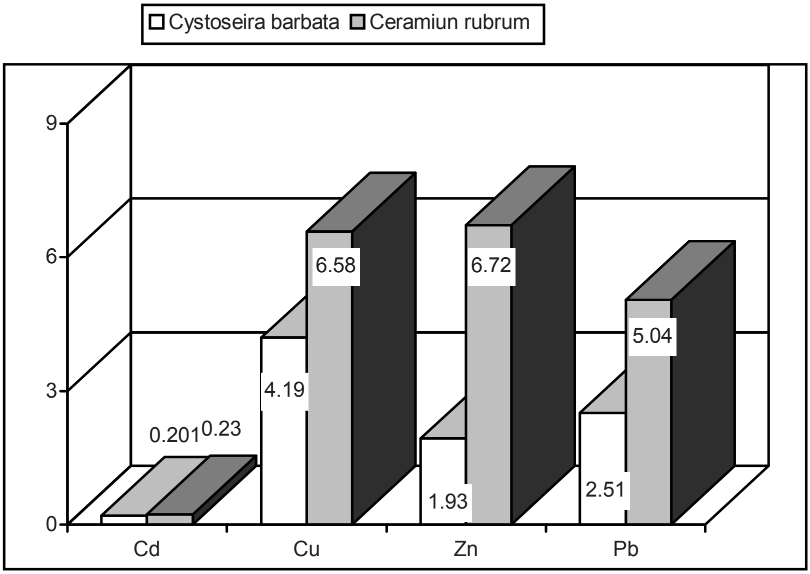

Figure 1. Heavy metals concentrations in marine algae from Romanian Black seacoast in 2007 (mean values, µg/g).

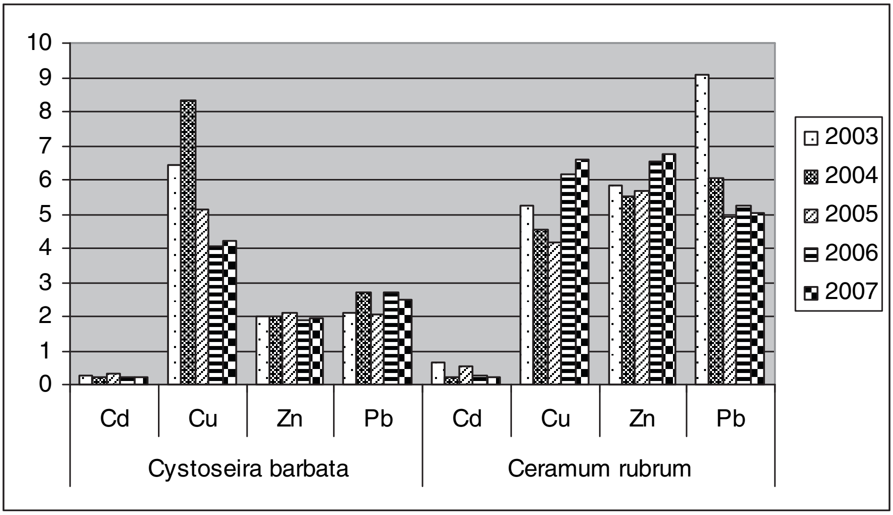

Figure 2. Comparative results of heavy metals concentrations in marine algae from Black seacoast in the last 5 years (mean values, µg/g).

TABLE 1. Organochlorine pesticides concentrations in marine algae from Romanian Black seacoast in 2007 (mean values, μg/g).

Organochlorine pesticide	Retention time (min)	*Cystoseira barbata*	*Ceramium rubrum*
α-HCH	8.049	ND	ND
β-HCH	9.622	ND	ND
γ-HCH	10.930	0.02228	0.0276
δ-HCH	11.100	ND	0.0122
Aldrin	17.846	ND	ND
Heptaclor	16.365	ND	ND
Dieldrin	22.074	ND	ND
Endrin	22.974	ND	ND

ND – not detectable.

A hazardous substance can be characterized as bioaccumulative when the bioconcentration factor is bigger than 2,000 (Arnot and Gobas, 2006). The bioconcentration factors (BCF) for the studied contaminants in both algae are presented in Figure 3.

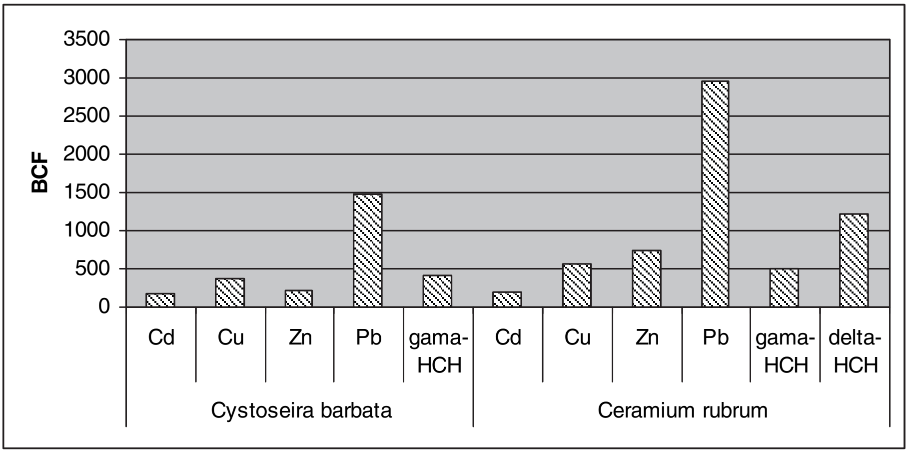

Figure 3. Bioconcentration factors in marine algae from Romanian Black seacoast in 2007.

Our results show that only lead in *Ceramium rubrum* has a BCF value over 2000.

4. Conclusions

The obtained results demonstrate that the analysed algae can be used as raw material for pharmaceutical purposes without risks for human health, considering the low concentration levels of contaminants.

Bioaccumulation abilities for heavy metals as well as for organochlorine pesticides are higher for red algae *Ceramium rubrum* than for brown algae *Cystoseira barbata*. This fact can be explained by the habitat on the sea level or by the specific metabolism of each algae.

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NOVEL DAPHNIA TEST FOR DETECTING CHEMICAL POLLUTION

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Abstract. *Daphnia magna* (water flea) is perhaps the most commonly used test organism. As they represent primary consumers in freshwater aquatic ecosystems, their relevance in screening bioassays is very high. However, performing the standard *Daphnia* mortality test requires a 24–48 h exposure time, therefore no rapid response can be acquired on the risk posed by any environmental contamination. A novel bioassay has been elaborated and tested in our laboratory, using the above mentioned *Daphnia* species, but based on another ecological effect, the inhibition of feeding activity. Applicability and sensitivity of the test was assessed using potassium dichromate. Standard *Daphnia* test was also carried out as reference. The sensitivity range of the new method was similar to the reference test (EC_{50} was in the same magnitude in comparison to *Daphnia magna* mortality test). Its further benefit is that this bioassay is using a sublethal endpoint.

Keywords: Daphnia magna, ecotoxicity, bioassay, environmental contamination

1. Introduction

Ecotoxicological tests are widely used for assessing the risk of environmental contaminants. They measure the aggregate toxicity of the sample and also, give an indication whether the contaminants are in bioavailable form. One key component of quality assurance is ecological relevance, that is, an ideal test organism represents an important structural and/or functional element of the ecosystem impacted. That is why daphnids are perhaps the most commonly used test organisms: they occur world-wide and also, they have a key role in aquatic ecosystems, providing important food for fish.

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The ISO 6341:1996 standard uses *Daphnia magna* Straus, the end-point of the test is the inhibition of motility (practically mortality). This is an acute toxicity test, where the exposure is 24–48 h. In order to avoid the laborous work of maintaining a stock culture, the Laboratory for Biological Research in Aquatic Pollution (LABRAP) of the University of Ghent has developed so-called toxkits which contain the test organisms in dormant form (such as eggs or cysts) (Persoone, 1996). Several kits are available for representing zooplankton organisms, such as the THAMNOTOXKIT F^{TM} (24 h acute toxicity test with the anostracan crustacean *Thamnocephalus platyurus*), the CERIODAPHTOXKIT F^{TM} (24 h acute toxicity test, based on the cladoceran crustacean *Ceriodaphnia dubia*), the DAPHTOXKIT F^{TM} magna (24–48 h acute toxicity test, based on the cladoceran crustacean *Daphnia magna*) and the DAPHTOXKIT F^{TM} pulex (24–48 h acute toxicity test, based on the cladoceran crustacean *D. pulex*). The DAPHTOXkits contain dormant eggs, ephippia, which normally serve for surviving in unfavourable environments. When an assay is to be carried out, neonates are hatched in about 4 days from the eggs and used in the test.

Still, toxkit protocols describe the performance of mortality tests. However, mortality is an ultimate and non-specific endpoint, its relevance to predict ecological risk can be questioned. In mortality tests toxicity of the sample is most often expressed in the form of EC_{50}.

Daphnids can show other symptoms which are relatively easy to assess and give an earlier warning of the toxic effect. Lotocka (2003) tested the grazing intensity of the daphnids with respect to two species of cyanobacteria, *Microcystis aeruginosa* and *Aphanizomenon flos-aquae*. Rohrlack et al. (2004) followed molting disruption caused by cyanobacterial toxins and found that affected individuals were unable to shed the old integument although a new integument had been produced.

The Daphnia Toximeter of bbe moldanke is a measuring device with constantly running sample water. Movement pattern of daphnids are recorded such as average speed, turns, circling movements, etc. The live images are analysed online and any changes in the behaviour are immediately evaluated.

The IQ Toxicity Test™ kit for grab samples developed by Aqua Survey, Inc. is based on fluorescent tagging and metabolism of organisms. In the presence of toxins, the metabolism of *Daphnia magna* is reduced, blocking their normally visible light emittance. For performing the test daphnids are first fed on a fluorescent sugar reagent.

Life-history traits such as somatic (individual) growth (Burks et al., 2000), time to first reproduction, number of newborns can also be studied (Lürling and van der Grinten, 2000). Lürling (2001) used population growth as the measure of toxic effect.

Biochemical end-points such as inhibition of in vitro protein phosphatase activity can also be used and quantified (De Mott and Dhawale, 1995).

Daphnia heart beat rate tests are measuring the changes of the heart beat rates of daphnids during the exposition. This method was used very early by E. R. Baylor, in 1942. At room temperatures the heart beat of Daphnia is too rapid to count with the naked eye. Therefore a stroboscope is devised to measure the cardiac rate at these higher temperatures. In other experiments the specimen are cooled to 10°C and the heart is counted by eye (Baylor, 1942).

These assays and test end-points provide a novel approach to study ecological response of daphnids other than mortality, however, some of them are difficult to quantify. A bioassay based on the feeding activity of *D. magna* was developed in the Ecotoxicological Laboratory of the University of Pannonia. The test gives quantifiable results and therefore it can be standardised. Our aim was to validate this new method, proving it is sensible enough to replace the standard mortality test. For this purpose, different exposure regimes (1, 2 and 4 h) were set, ecological effects were measured and quantified and finally compared to results of the conventional 24-h bioassay.

2. Materials and Methods

2.1. SOLUTION PREPARATION

For preparing test samples, first 19.82 mg/ml standard solution was made from $K_2Cr_2O_7$, than a 1:2:4:8:16 dilution series was made using standard freshwater.

2.2. ASSESSING OF DAPHNIA FEEDING ACTIVITY

The DAPHTOXKIT F^{TM} magna kits were purchased from the MicroBioTests Inc. Each kit contains the dormant eggs of *D. magna*, disposable labware and also, solutions for preparation of standard freshwater. This standard freshwater is used for hatching the ephippia. Hatching takes place in app. 4 days and requires an incubator with continuous illumination of 10,000 lux and temperature of 20°C.

The test was carried out in so-called microplates (Figure 1). Each cell was filled with 10 ml *(D. magna)* sample solution, for control standard freshwater was used. The test was performed in three replicates. After preparation of the microplate, ten *D. magna* test organisms were transferred to each cell, using a micropipette. Three different contact times were applied: 1, 2 and 4 h. During exposure, microplates were kept in the incubator at 20°C but in darkness. After exposure, larvae were fed with a suspension of red microspheres for half an hour. During feeding, microplates were kept again in the incubator at 20°C in darkness.

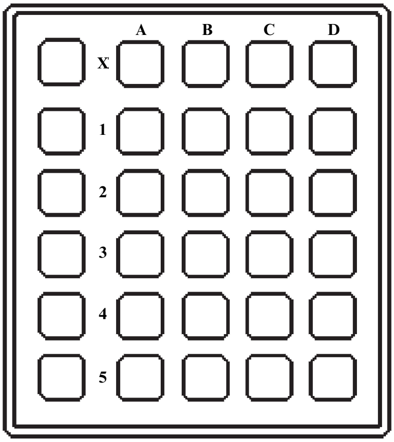


Figure 1. Microplate for performing the *Daphnia* test. x: control; 1–5: test concentrations; A–D: replicates.

After incubation a fixative was added, and dead larvae were visually assessed under stereomicroscope. Number of those larvae was counted which contained red microspheres in their digestive tracks (Figure 2 shows normally feeding larvae, which develop dark coloured digestive track).

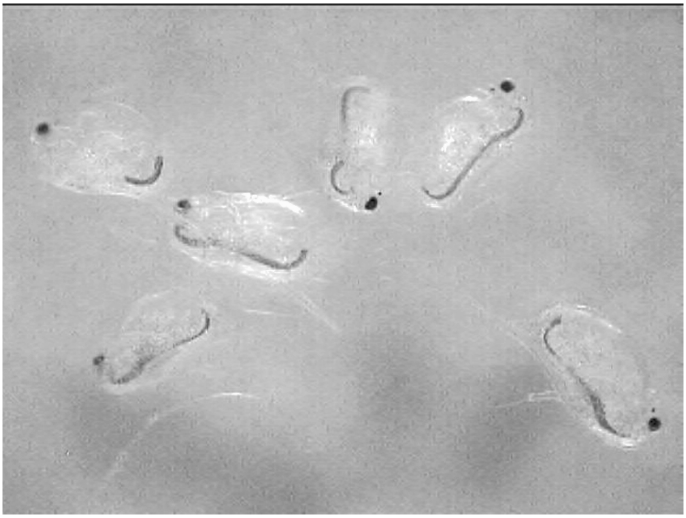
Ecological effect was expressed as percentage of impacted individuals.

3. Results and Conclusions

Measurable end-point of the test was the number of individuals which did not show red (dark) digestive track, that is, their feeding activity was inhibited by the toxicant. These raw data were used for calculating EC_{50} values (this is the hypothetical concentration which would cause 50% effect). EC_{50}s were determined by the Probit software developed by USEPA. Table 1 shows EC_{50} values, in mg $K_2Cr_2O_7$/ml. Standard *D. magna* mortality tests were carried out for reference, results of the feeding activity inhibition bioassays are compared to those.

Tests using 1 h exposure were not able to provide visible results. Significant effect (inhibition) could be observed after 2 and 4 h contact time. After 4 h exposition, this method shows a very good correlation to the 24-h mortality test.

Figure 2a. Normally feeding *Daphna* against normal background.



Fiigure 2b. Dark (red) digestive tracks of normally feeding *Daphnia* against a blue background, which gives a higher contrast: red microspheres are more visible but disturbing visual effect of inner organs of the animals is minimized.

This novel bioassay described here is able to represent the potential response of *Daphnia magna* to environmental contaminants. As contact time is significantly shorter, in some cases it might replace the traditional mortality test. However, in order to determine its overall sensitivity, a wide range of environmental samples have to be tested.

TABLE 1. Results of feeding activity inhibition bioassays, using mortality tests as reference.

	EC_{50} mg/ml *D. magna*
Feeding activity inhibition, exposure 1 h	–*
Feeding activity inhibition, exposure 2 h	6.09
Feeding activity inhibition, exposure 4 h	1.74
Mortality, exposure 24 h	1.09

* No inhibition was observed, all larvae were feeding normally.

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FLOOD RISKS IN AGRICULTURAL AREAS ALONG MESTA RIVER

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Abstract. Natural hazards and flood events are part of nature. In most cases, floods are caused by climatological phenomena, which are out of human control. The scale and frequency of floods are likely to increase in the future as a result of climate change, inappropriate river management and construction in flood risk areas. There has been a marked increase in vulnerability due to the number of people and economic assets located in flood risk zones. Two natural disasters such as drought and flood have effected on different parts of the earth as a result of increasing human's interference on global climate. In the recent years, our country was a witness in occurrence of floods and severe droughts, which has caused destruction of agricultural lands. The process of the delimitation of the endangered agricultural areas is a priority task for the Bulgarian scientists and the Water authorities. A research of the river basin of Mesta concerning such flood issues has been carried out. Hydrological analyses were made in order to get the probability of the maximum runoff. The obtained results were considered in different scenarios of flood events (water level or depth, flood extends), meeting the requirements of the European Union (EU) Flood Risk Management Directive. The presented research is a part of a project for young scientists about determination of the agricultural areas endangered by floods in the river Mesta watershed.

Keywords: flood risk assessment, maximum runoff, hydrology, flood risk management directive

The Floods Directive 2007/60/EC on the assessment and management of flood risks entered into force on 26 November 2007. The objective of the Flood Directive is to reduce and manage flood-related risks to human health,

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environment, infrastructure and property. It has to provide for flood mapping in all areas with significant flood risks, for coordination within shared river basins, and for elaboration of flood risk management plans through a broad participatory process. The management of flood risks is a crucial component of climate change adaptation, and the Directive requires from the member States of EU to take climate change into account in the preliminary flood risk assessment. The proposed legislation intends to complement the Water Framework Directive (WFD) as regards to flood risk management, and focuses on prevention, preparedness and protection measures. Close coordination with the WFD is foreseen, in particular regarding the plans, which have to be prepared in synchronisation and coordination with River Basin Management Plans (RBMP).

1. Introduction

The currently existing norms in Bulgaria dimensioning the water structures along the river stream are subjected to reconsideration taking into account the floods in 2005. In respect to this the present research deals with some scenarios for different probability of exceedence. It is important to be known the discharge corresponding to the certain probability of exceedence. Hydrological studies are necessary in order to obtain the probability curves of exceedence of the maximum annual discharges for each section endangered by flood. From hydraulic point of view the conditions have to be assessed for a certain discharge which will flow through a defined water sections without overflowing. An evaluation by geodetic survey for the cross-sections showing the current state is needed for the establishment of a numerical model for river capacity in the areas of flood risk.

2. Basic Watershed Characteristics

Mesta is a transboundary river situated in the South-West part of Bulgaria (Figure 1) with catchments area of 2,768 km^2 or more than 3,150 km^2 including the Dospat river basin. It has an abundance of water and forests. The Mesta river runs from north to south and has a length of 126 km up to the Greek border and about 140 km within Greece. Its largest tributary is the river of Dospat with a length of 82 km to the border, where it flows into the river Mesta in Greek territory. The upstream valleys of the two rivers are steep and narrow (Bournazki, 2005).

The Mesta river and its tributaries are fed by the numerous lakes and springs. The Mesta valley is between the mountain Pirin to the west, Rodhopi to the east and Rila mountain – to the north (the highest on the Balkan peninsula).

The annual mean runoff from the Bulgarian part of Mesta river basin, measured close to the border according to the latest assessments (Marinov et al., 1979) amounts to 11,00,106 m^3. It is one of the richest with waters basins in Bulgaria with the highest average level above the sea – 1,310 m.

At present there are three small irrigation systems – "Razlog" (1,200 ha), "Gotze Delchev" (4,130 ha) and "Ablanitza-Varcosel" (673 ha) with intakes from Mesta and some tributaries. The main sources for water supply are intakes from small rivers and catchments situated high in the mountain (General schemes of water use in the river Mesta watershed, 2000).

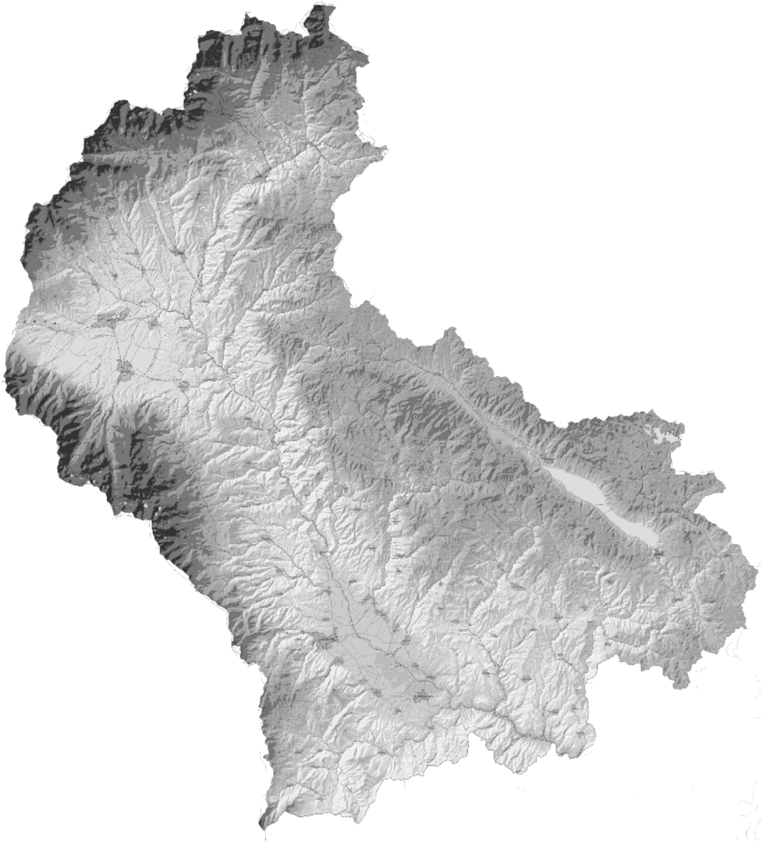

Figure 1. A map of the watershed of the river Mesta.

The monitoring in Mesta river watershed is accomplished by 22 gauging stations and the following hydrological stations are on the main stream: Iakoruda – situated in the upper part of the watershed, Momina kula – in the middle part and Hadjidimovo – downstream. The research is focused on the flood hazards of agricultural areas, particularly on the main river – around the town of Iakoruda – upstream and the village of Hadjidimovo – downstream. Hydrological analysis has been conducted for both stations (Iakoruda and Hadjidimovo). Time series of observed maximum annual discharges for period of 55 years and respectively 51 years have been used.

3. Hydrological Analysis

3.1. FORMATION OF THE SEQUENCES FOR THE BASIC HYDROLOGICAL STATIONS

The calculus of probability and mathematical statistic are used for the hydrological analysis. The statistical methods in hydrology are used successfully for solving many problems concerning the formation of the maximum runoff and its characteristics. This method is based on the observed historical data of monthly discharges (average, maximum and minimum) at Iakoruda – 1951–2005 and Hadjidimovo – 1955–2005. The available runoff observation data as a whole is limited. The length of the runoff sequence (n) is 40–50 years. Special feature exists in determining the characteristic of the maximum runoff with lower probability (once at 100, 1,000, 10,000 years). Empirical probability exceedence curve does not allow extrapolations in zone $P \leq 100\%$. This imposes wider use of the several mathematical methods.

3.2. INVESTIGATION OF THE HOMOGENEITY

The representativeness of the available hydrological sequences is assessed by investigations related to establishment of the homogeneity and belonging to the members of the hydrological sequences of the general populations. This is made by the means of two nonparametric criteria of Wilcoxon and Kolmogorov-Smirnov. After the investigations of both sequences of Iakoruda and Hadjidimovo non-homogeneity was established. The statistical non-homogeneity is in consequences of disturbance of the natural regime of the runoff. In this case were registered 113 disturbances at hydrological stations Hadjidimovo according to (Reference book of the rivers in Bulgaria, 1981).

3.3. EVALUATION OF THE STATISTICAL PARAMETERS

The available short-term observations and considerable variability of the runoff leads to essential difficulties in assessment of the parameters of one-dimensional runoff distributions. In this relation arises one of the basic problems when carrying out hydrological research, in particular by determination of effective methods for parametric assessment (Ivanov and Peneva, 2003). The statistical parameters of the maximum runoff were assessed by the method of moment, together for three types of distribution functions: lognormal 2-parameter, lognormal 3-parameter (3LOG) and Pearson III. The investigations results are given in Tables 1 and 2 for both hydrological stations.

TABLE 1. Statistical parameters of hydrological station № 207 “Iakoruda”.

MM (method of moments)			MM-LSM (least squares method)			
Lognormal 2-parameter distribution			Lognormal 3-parameter distribution		Pearson III	
Parameter		x		z = x – a	Mean value	35.54
Mean value	Mx	35.540	z_	33.058	Cv_x	0.811
Standard deviation	σ	28.810	σ_z	28.810	Cs^{LSM} P-III	2.731
Variance coefficient	Cv	0.811	Cv_z	0.871		
Asymmetric coefficient	Cs	2.585	Cs_z	2.585		
Excess	Es	8.271	Es_z	12.507		
			Optimized parameter ***a*** (LSM)	–2.482		
Dispersion	Su^2_λ	0.502	σ_u^2	0.695		
	Z_	35.618	Z_	34.320		
	$\sigma_x = \sigma_z$	28.770	$\sigma_x = \sigma_z$	34.370		
	Cv_z	0.808	Cv_z	1.001		
Mean value	Xo_λ	35.618	MX	36.802		
Variance coefficient	Cv_λ	0.808	Cv_x	0.934		
Asymmetric coefficient	Cs_λ	2.950	Cs_x	4.009		

TABLE 2. Statistical parameters of hydrological station № 230 “Hadjidimovo”.

MM (method of moments)			MM-LSM (least squares method)			
Lognormal 2-parameter distribution			Lognormal 3-parameter distribution		Pearson III	
Parameter		x		z = x – a	Mean value	258.1
Mean value	Mx	258.06	z_	256.86	Cv_x	0.624
Standard deviation	σ	161.09	σ_z	161.09	Cs^{LSM} P-III	1.832
Variance coefficient	Cv	0.62	Cv_z	0.62		
Asymmetric coefficient	Cs	1.596	Cs_z	1.596		
Excess	Es	2.56	Es_z	2.55		
			Optimized parameter ***a*** (LSM)	6.10396		
Dispersion	Su^2_λ	0.502	σ_u^2	5.374		
	Z_	35.618	Z_	0.364		
	$\sigma_x = \sigma_z$	28.770	$\sigma_x = \sigma_z$	258.618		
	Cv_z	0.808	Cv_z	171.269		
Mean value	Xo_λ	35.618	MX	0.662		
Variance coefficient	Cv_λ	0.808	Cv_x	259.808		
Asymmetric coefficient	Cs_λ	2.950	Cs_x	0.659		

4. Determination of the Theoretical Probability Exceedence Curve

The theoretical probability exceedence curve describes the runoff fluctuations in a general population. As it was mentioned above in this research are used three distributions: two lognormal and distribution of Pearson III (Nikolova, 1979). Due to the high asymmetry the most suitable for describing the maximum runoff is provided to be the lognormal distribution. Distribution of Pearson III is three-parametric and allows expressing the fluctuation of runoff with a high variability (Table 3).

TABLE 3. Theoretical distribution functions of probabilities.

Theoretical distribution function	Density distribution function (density curve)
Three-parametric lognormal distribution	$p(z,z_o,\sigma_u)=\frac{1}{z.\sigma_u\sqrt{2\pi}}\exp\left(-\frac{\left(\ln\left(\frac{z}{z_0}\right)-\frac{\sigma_u^2}{2}\right)^2}{2\sigma_u^2}\right)$ $z\in(0;+\infty)\quad z=x-a;\quad \bar{z}=\bar{x}-a\quad u=\ln(x-a)=\ln(z)$
Two-parametric lognormal distribution	The same equation as three-parametric lognormal distribution, when parameter ***a*** = 0
Pearson III	$p(x,x_o,\gamma,l)=\frac{\gamma^{\gamma}}{\Gamma(\gamma)(x_o-l)}\left(\frac{x-l}{x_o-l}\right)^{\gamma-1}.\exp\left[-\gamma\left(\frac{x-l}{x_o-l}\right)\right]$ $x>l$ $Cv=\left(1-\frac{l}{x_o}\right)\frac{1}{\sqrt{\gamma}}Cs=\frac{2}{\sqrt{\gamma}}Es=\frac{3Cs^2}{2}\frac{l}{x_o}=1-2\frac{Cv}{Cs}$

Empirical probability is calculated using Aleksiev's formula:

$$P(m)=\frac{m-a}{n+b}$$

$$a=\frac{n+1-\sqrt{n(n+1)}}{2};\quad b=\sqrt{n(n+1)}-n$$

Different theoretical probability exceedence curve have been applied and tested for fitting. The results are shown in Figures 2 and 3.

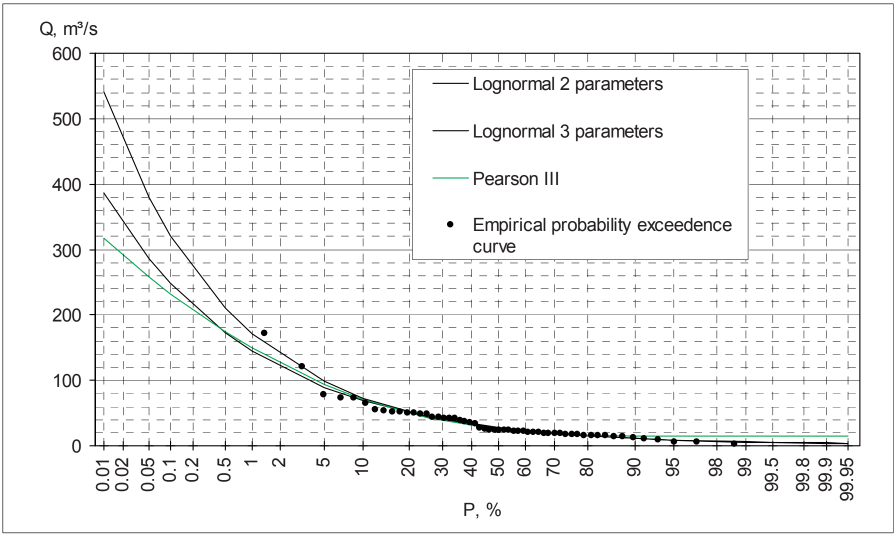

Figure 2. Theoretical probability exceedence curve "Iakoruda".

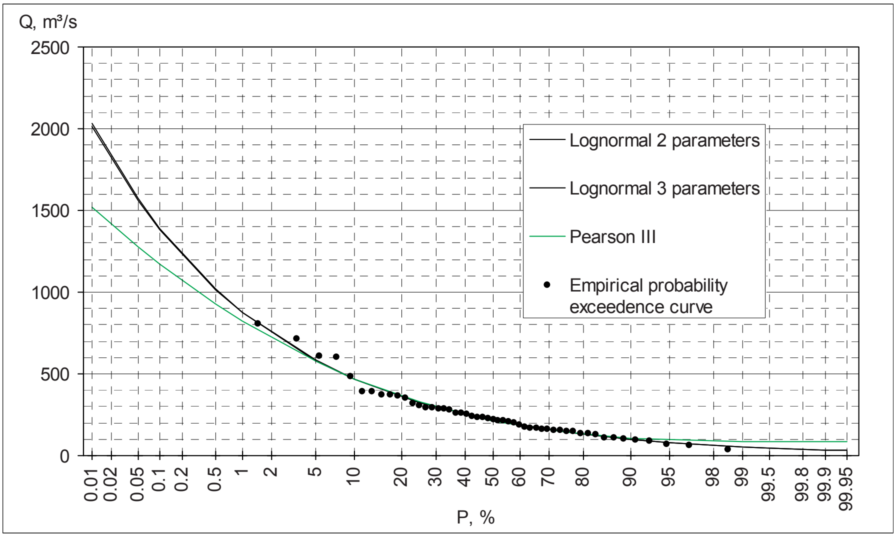

Figure 3. Theoretical probability exceedence curve "Hadjidimovo".

5. Choice of the Most Suitable Theoretical Probability Exceedence Curve

The choice of the most suitable theoretical probability exceedence curve is one of the basic tasks of the hydrological investigations. The analyses for choosing the most suitable theoretical probability exceedence curve are carried out by the means of one of the most reliable criterion of concordance, namely $n\omega^2$ (Marinov et al., 1980).

$$n\omega^2 = \sum_1^n [\frac{P_E(x_i) - P_T(x_i)}{100}]^2$$

for the short-term sequences is accepted:

$$\sum_1^n \Delta Q^2 = \sum_1^n (Q_E - Q_T)^2 = \min,$$

where the formula is transformed in:

$$\sum_1^n \Delta Q^2 = \sum_1^n (Q_E - Q_T)^2 = \min$$

The results of comparison are shown in the Table 4, in the last column is pointed out the choice of the theoretical probability exceedence curve.

TABLE 4. Choice of theoretical probability exceedence curve.

Hydrological stations	LOG3	Pearson III	Choice
Iakoruda	5.496	6.54	LOG3
Hadjidimovo	21.04	24.42	LOG3

6. Evaluation of the Discharge for High Waters with Probability of Exceedence – 5%, 1% and 0.1%

Floods analysis was carried out by the use of maximum annual discharges time series.

Discharges for the standard probability of exceedence are given in Tables 5 and 6 and the corresponding discharges to the chosen probability of exceedence are highlighted.

TABLE 5. Theoretical probability exceedence curve of “Iakoruda” gauging station.

P_T %	LOG2	LOG3	Pearson III
0.01	386.62	540.57	317.66
0.05	285.36	378.97	257.90
0.1	247.59	**321.08**	232.40
0.5	171.95	210.00	173.94

1	144.09	**171.04**	149.21
5	88.89	**98.00**	93.50
10	68.71	73.04	70.70
25	44.69	45.03	43.36
50	27.71	26.73	24.62
75	17.18	16.30	17.01
90	11.17	10.82	14.89
95	8.64	8.64	14.58
99	5.33	5.97	14.48
99.5	4.46	5.32	14.48
99.9	3.10	4.33	14.47
99.95	2.69	4.04	14.47

TABLE 6. Theoretical probability exceedence curve of "Hadjidimovo" gauging station.

P_T (%)	P_T (%)	P_T (%)	P_T (%)
0.01	2,011.94	2,032.16	1,520.28
0.05	1,556.65	1,569.65	1,278.60
0.1	**1,380.72**	**1,391.19**	1,174.00
0.5	1,014.72	1,020.46	930.22
1	873.93	**878.09**	824.70
5	581.13	**582.59**	577.74
10	467.53	468.20	470.04
25	325.06	325.04	328.40
50	217.06	216.81	211.98
75	144.94	144.76	141.98
90	100.78	100.74	107.12
95	81.08	81.16	95.74
99	53.91	54.21	85.89
99.5	46.43	46.80	84.46
99.9	34.12	34.64	83.16
99.95	30.27	30.83	82.97

6.1. HYDRAULIC MODELING

Hydraulic computations have to be carried out for determination of the endangered from inundation agricultural areas along the Mesta River. These computations will be conducted by HEC-RAS software package. The computations are based on the energy equation solved by standard step method from one section to the next.

Hydraulic modeling will be performed based on geodetic survey and hydrometric measurements of the investigated river sections.

Cross-section profiles from maps 1:500 and geodetical measurements will be used for the modeling. Positions of the cross-sections in the studied part of the river between the towns Goce Delchev and Hadjidimovo are chosen according to the existing bumps.

7. Conclusions

The current study is a basic part of a research project carried out in accordance with the Flood Directive. The obtained values for exceedence of probabilities have served for running different scenarios. In the paper three probabilities of exceedence values (5%, 1% and 0.1%) are emphasized but the scope of the values could be reconsidered. According to the requirements for flood protection of agricultural lands, the flood with certain probabilities can be accepted as effective discharge for dimensioning the flood plain. These results are a base for hydraulic computations and preparation of flood maps for the studied agricultural lands.

The watershed of Mesta River needs an alternative and proper management reducing the effects and damages from flood. This research is expansible and usable for other similar river basins.

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ASSESSMENT OF LAND POLLUTION AND POLICY ANALYSIS FOR SECURE DEVELOPMENT STRATEGIES IN ARMENIA

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Abstract. Environmental security and sustainability is a major issue for development of Eastern European and post-soviet countries. Economical development and technological change must be balanced with effective environmental solutions. Secure and sustainable development in is connected with several, mostly common problems. In Armenia secure development policies are focused on several problems: Economic and social problems specific to countries in transition (overall decline of economic activities, severe budget constraints, high domestic and foreign indebtedness, institutional weakness, etc); Geopolitical instability (neighborhood problems, blockade, ethnic wars, political upheavals, etc) and their impact on environment; Soil degradation and desertification; Unequal distribution of water resources; Deforestation problems; High occurrence of natural disasters. Armenia is stepping towards implementation of secure development strategies and has real shifts, meanwhile on the way to sustainable solutions there are several underlined obstacles. The paper is focused on the analysis of current situation with legal and institutional framework and development policies. Nowadays soil degradation and desertification are key problems for the Republic of Armenia. The problem of desertification in Armenia, on which is focused the paper, is a typical case, around which the process of secure development in the region could be observed.

Keywords: secure development, land pollution, chemical pollution, desertification, environmental management, environmental legislation, land privatization

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L.I. Simeonov and M.A. Hassanien (eds.), *Exposure and Risk Assessment of Chemical Pollution - Contemporary Methodology*,

1. Introduction

In developing world the aim of transition is not only to improve economic performance in the short and the long term but also to move towards secure and sustainable development. In Post-Soviet countries, particularly in Armenia, a set of environmental problems are aggravated. These problems have severely threatened the sustainable development of these countries and have caused great concern at all levels, from the general public to national governments and international agencies.

The efforts of these countries to strengthen the institutional capabilities for environmental policy-making, planning and management, are being undermined by numerous weaknesses, deficiencies and difficulties, such as weak or inadequate legislation, the lack of political clout of environmental authorities, low public awareness, lack of well established target groups which represent specific interests, the lack of managerial skills, the inadequate information base, not to mention the general lack of financial resources.

The problems of land resources are more important for the countries with scarcity of land recourses. Nowadays land degradation and desertification are key problems for the Republic of Armenia. Armenia is situated in the South of the Caucasus and occupies only 29.8 km^2. The process of desertification includes 80% of the Republic's territory. In addition to the above-mentioned negative tendency, the new factors came to the science over the last few years, such as ineffective land utilization as a result of privatization, cut backs of financial resources directed against droughts and for building of water construction objects, decrease of necessary activities controlling the sphere of urban construction and planning, and measures aimed at prevention of land degradations due to the intensive exploitation of mines.

2. Political, Legal and Institutional Framework

Setting up effective political, legal and institutional framework of secure development is a major issue for most of developing countries. Political, legal and institutional solutions must be integrated in one effective working system in order to support secure development. In Armenia, after transformation period, there are notable achievements in this area, particularly in the spheres of environmental legislation and international cooperation, but there are also a set unsolved problems, which are in the center attention of the government.

In 1991, the newly independent Armenia entered a period of radical changes that involved political, social, and economic systems. The transition period started with a drastic economic and energy crisis, and the accompanying transportation blockage resulting from regional conflicts. The economic decline resulted in some 800,000 people (out of Armenia's population of 3.8 million) leaving the country. Economic growth restarted in 1994 and has continued to the present at a high rate, averaging 6–8% due to macroeconomic stabilization, and the adoption of a liberal model of economic and trade regulation. Poverty in Armenia, and particularly the number of very poor, has diminished.

2.1. MAJOR ACHIEVEMENTS AND CHALLENGES

Evidence shows that environmental management has improved over the last decade in Armenia. Policy objectives have been clarified, strategies to achieve them are being developed, and additional resources are provided to support the system of environmental management. The main environmental authority – the Ministry of Nature Protection (MNP) – has enjoyed structural stability and preserved the integrated scope of its mandate that covers both use of natural resources and pollution prevention and control.

Particularly impressive is Armenia's success in improving the legal basis for compliance assurance, and efforts made since 2003 to raise the quality of regulatory design. Armenia's main environmental enforcement authority, the State Environmental Inspectorate of the Ministry of Nature Protection (SEI), has the responsibility to check and ensure compliance with requirements related to the use of natural resources, industrial pollution, and other environmental impacts. Recently, priority environmental objectives covering the rational use of mineral and forest resources, managing the ecosystem of Lake Sevan, and waste management, were included in the Poverty Reduction Strategy Paper (PRSP).

Notwithstanding these significant achievements, Armenia has yet to address a number of challenges about which the SEI is fully aware and prepared to address. The unresolved problems requiring urgent attention include:

- The environmental regulatory framework is still incoherent; environmental quality standards and permit requirements tend to be unfeasible and difficult to enforce. This undermines the rule of law and public confidence in the government's capacity to regulate.
- Incentives for regulates to comply and improve environmental performance are low.
- The Inspectorate uses only a small number of the legally available tools to ensure compliance.
- The institutional capacity of the Inspectorate, particularly of its regional agencies, is low due to lack of training, imperfect staff selection approaches, and prolonged and heavy shortage of resources.
- Cooperation with other stakeholders, both domestically and internationally, is limited and sporadic.

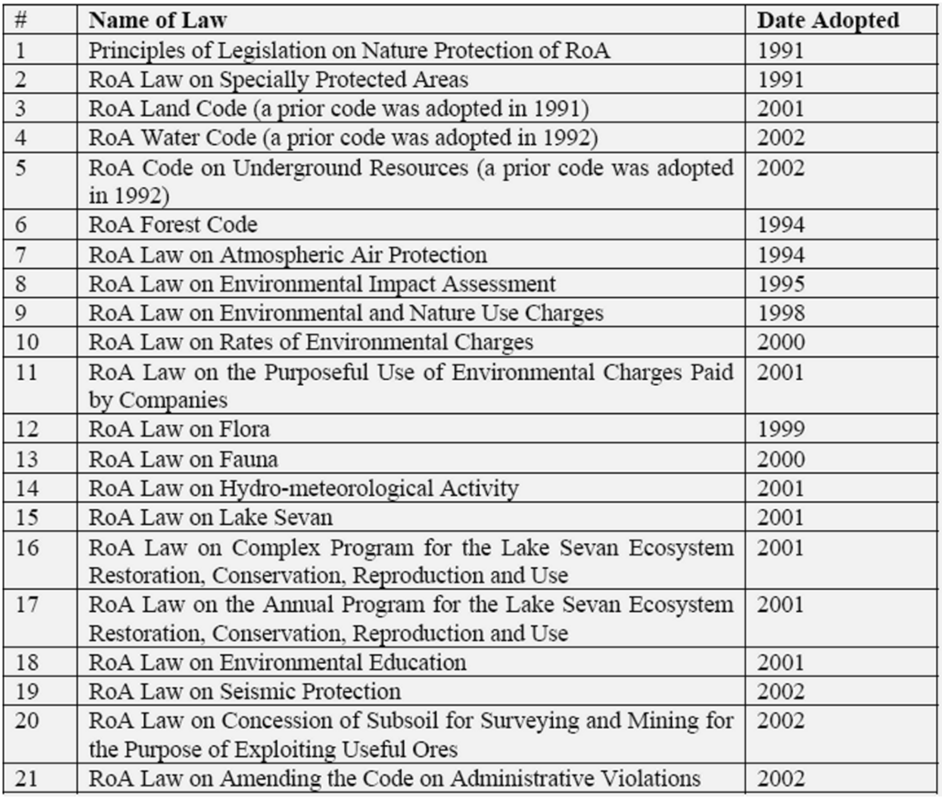
As a result of environmental management reform, a whole range of policy instruments is already in place and includes, besides traditional command-and-control instruments, economic instruments. Also enforcement tools, such as monetary penalties, were reformed to provide a stronger deterrent effect. The next planned step is to adopt instruments that make better use of market incentives and involve consumers and investors in the process of awarding good environmental performance and penalizing non-compliance.

Environmental authorities in Armenia focus their efforts on the following priorities of institutional development:

1. Streamlining the regulatory framework and making it feasible
2. Optimizing the use of powers, vertical structure, and cooperation with other agencies
3. Increasing transparency of inspection and mutual understanding with the non-governmental sector
4. Using compliance assurance tools more effectively
5. Actively mobilizing necessary resources
6. Capitalizing on opportunities for international cooperation

2.2. ENVIRONMENTAL LEGISLATION IN ARMENIA

Following the World Summit on Environment and Development that took place in Rio de Janeiro in 1992, at which a number of multilateral environmental agreements were adopted and signed, the Republic of Armenia has signed and ratified 13 environmental conventions and six associated protocols. The authorized state agency for the aforementioned conventions is the Ministry of Nature Protection of the Republic of Armenia. Since independence was proclaimed, the Republic of Armenia has adopted a number of laws in the sphere of nature protection, as these were dictated by the new political and economic realities. Many of them are directed at the implementation of obligations under conventions signed. The basis of environmental legislation was formulated after the Summit in Rio. Article 10 of the Constitution of the Republic of Armenia guarantees protection of the environment by the state, as well as the rational use and renewal of natural resources (Constitution, 1997). Currently, four codes and 17 laws on the environment and related sectors are in force in the Republic of Armenia. They are:



#	Name of Law	Date Adopted
1	Principles of Legislation on Nature Protection of RoA	1991
2	RoA Law on Specially Protected Areas	1991
3	RoA Land Code (a prior code was adopted in 1991)	2001
4	RoA Water Code (a prior code was adopted in 1992)	2002
5	RoA Code on Underground Resources (a prior code was adopted in 1992)	2002
6	RoA Forest Code	1994
7	RoA Law on Atmospheric Air Protection	1994
8	RoA Law on Environmental Impact Assessment	1995
9	RoA Law on Environmental and Nature Use Charges	1998
10	RoA Law on Rates of Environmental Charges	2000
11	RoA Law on the Purposeful Use of Environmental Charges Paid by Companies	2001
12	RoA Law on Flora	1999
13	RoA Law on Fauna	2000
14	RoA Law on Hydro-meteorological Activity	2001
15	RoA Law on Lake Sevan	2001
16	RoA Law on Complex Program for the Lake Sevan Ecosystem Restoration, Conservation, Reproduction and Use	2001
17	RoA Law on the Annual Program for the Lake Sevan Ecosystem Restoration, Conservation, Reproduction and Use	2001
18	RoA Law on Environmental Education	2001
19	RoA Law on Seismic Protection	2002
20	RoA Law on Concession of Subsoil for Surveying and Mining for the Purpose of Exploiting Useful Ores	2002
21	RoA Law on Amending the Code on Administrative Violations	2002

Certain elements of the environmental policy are formulated in the National Environmental Action Plan (NEAP, 1997) and in the Action Plans within the framework of the environmental conventions' implementation and relevant strategies: "National Action Plan on Desertification in Armenia" (2002), "Biodiversity Strategy in Armenia and the National Programme of Action" (1999), "National Programme of Phase-Out of the Ozone-Depleting Substances", "Integrated Water Resources Management Programme" (2001), "National Programme of Actions of the Republic of Armenia on Persistent Organic Pollutants" (at a drafting stage), etc. In general, all above listed political documents were developed after 2000. As to NEAP (in force since December 1998), it is important to note that in 2004 the National Environmental Action Plan has been revised and the monitoring of the implementation has been conducted. The Action Plan has been overall implemented, however it turned out that over the years after its adoption, some changes in priorities in environmental area took place, and there is a necessity of the re-orientation to more effective solutions. In view of the above, there is a need to develop a new National Environmental Action Plan based on the achieved results, new priorities and approaches.

2.3. MANAGEMENT ISSUES

Environmental activities in the country are carried out according to the international obligations and country's legislation. International agreements ratified over the last years, in addition to those which the country had acceded to earlier, strategies developed within the framework of their implementation, program, legal documents, and existing administrative structures, allowed to make this sector operational.

The State Committee on Water Management, established under the Government of the Republic of Armenia, deals with the system of *water* supply. New Water Code that was adopted in 2002, according to international experts is one of the most advanced in the region. Within the provisions of the Code, the National Water Council chaired by the Prime Minister of the Republic of Armenia, was established in September 2002. The establishment of the Agency of Water Resources Management within the Ministry of Nature Protection of the Republic of Armenia promotes the Water Code implementation. The Water Code stipulates provisions ensuring the participation of public organizations in protection and use of water resources. The law regulating supply and use of drinking water will be developed after having improved the necessary legal base.

In the area of *air* protection were improved the standards of air emissions of polluting substances based on the territorial principle approach and on technological standards approach according to the European practices. The improved methods on how to assess the damage to human health caused by the environmental pollutants and by the economic activities, including the "Concept of Reducing Air Pollution from Transport Emissions" have been developed and are proposed for consideration to the Government of the Republic of Armenia.

On *biodiversity* it is important to note that the Government of Armenia approved, by its decision in 2002, the "Strategy of Development of Specially Protected Areas of the Republic of Armenia and National Action Plan", which includes the improvement of the network of existing Specially Protected Areas (SPAs) and the establishment of new SPAs, as well as clarification of the Status of various SPAs.

2.4. INTERNATIONAL COOPERATION

International cooperation is one of the main conditions for solution of environmental problems of the country. According to EU/ARMENIA action plan one of the main priority areas for partnership is "e*ncouraging further economic development, thereby contributing to the long term objective of sustainable development, including the protection of the environment*".

Armenia's international cooperation in the environmental sphere has been shaped by the impulse of the World Summit in Rio, the first and the largest forum on environmental issues at which Armenia participated as a sovereign state. The principles of that forum established a basis for future actions in the sphere of environmental protection and sustainable development. At Rio, Armenia signed its first two international environmental conventions: the Convention on Biological Diversity and the Framework Convention on Climate Change. Later, Armenia joined a number of other environmental conventions. At present, Armenia has signed and ratified 14 conventions and nine protocols. In addition to participation in these conventions, Armenia's international environmental cooperation includes membership and participation in the programs of different international organizations (global and regional), such as the UN structures and the Council of Europe, which provide an opportunity for Armenia to participate effectively in international processes and present its interests. In general, Armenia's international environmental cooperation is determined by national priorities, geographical location, the necessity to solve jointly with other countries common environmental problems (at both regional and global scales), as well as by the domestic economic situation.

It should be mentioned that Armenia receives financial and advisory support from international financial organizations for the process of implementing global environmental conventions, at least at the stage of action plan and program development. In this regard, Armenia cooperates with GEF, UNEP, UNDP, World Bank and other organizations. Representatives of the Republic of Armenia have participated in large international forums and a number of working groups and commissions as a Party to regional and global conventions.

Since 2000, when the *Regional Environmental Centre (REC Caucasus)* was established, Armenia has actively participated in the activities of REC. The National Coordinating Unit of REC Caucasus has been created in Armenia.

3. Focusing on Desertification

Desertification is one of the global environmental issues of the Earth. Given the geological-climatic conditions Armenia is also subject to desertification and is greatly damaged, mainly due to land degradation, reduction of biodiversity and biological resources. Nowadays land degradation and desertification are key problems for the Republic of Armenia. Combating desertification is a strategic issue for republic (Association, 2002). Mitigation and prevention of desertification is a precondition for sustainable development of the country.

- About 24,353 km^2 of the territory of the Republic, 81.9% (excluding the surfaces of Lake Sevan and water reservoirs), are to different extents exposed to desertification: 26.8% of the total territory of Armenia faces extremely severe desertification; 26.4%, severe desertification; 19.8%, moderate desertification; and 8.8%, slight desertification. Only 13.5% (400 km^2) of the territory is not exposed to desertification.

- A "fast" process of desertification in Armenia is observed. In the period between 1950 and 1999, the area of arable land in Armenia decreased by 166,600 ha: meadows by 15,600 ha and pastures by 136,500 ha (National Statistical Service, 2006).
- Land recourses in Armenia are limited and land provision in Armenia is very low (0.13 ha of arable land per capita). The country is mountainous, with only 28% of land below 1,500 m altitude. According to this, loss of soil recourses even in small amounts is could have "heavy" influence on environmental sustainability.
- Desertification is a result of set of interrelated environmentally oriented problems-combating desertification means solution of many social, economical, regional problems.
- Agriculture is one of the main consumers of soil recourses and meanwhile the main "working" branch in Armenia with one third of domestic product and 42% of employment (Current Economic Problems, 2003).

The problem of desertification in Armenia is a good example, on the basis of which typical processes of balancing environment and development in East European countries and former soviet states could be observed.

3.1. IMPROVING THE NATIONAL POLICY

The "National Action Plan on Desertification in Armenia" mostly meets, by its essence and structure, the requirements of the "Convention to Combat Desertification" and may be considered as a national strategy, although it is important to find solutions of the following problems outlined in the Convention's 5th article.

- Shortage of adequate resources (material, human, and financial) which are necessary for anti-desertification actions and for elimination of consequences of droughts
- Specification of Republic's regional and local government authorities (based on their supremacy) and definition of deadlines for implementation of suggested activities

At the same time the "National Action Plan on Desertification in Armenia" is more macroeconomic by its nature; measures on fighting against desertification are not specified, problems of managerial authorities on the regional, branch and local levels are not divided; mechanisms which are necessary for monitoring of the program's implementation are not offered (Ministry of Nature Protection, 2003). The "Strategy on Sustainable Development of the RA Agriculture" has been developed in 2002 and defines the short and mid-term measures directed to develop this branch, including the ones related to the land use and land strategy (Strategy, 2002). However, it doesn't contain specific steps directed to prevent land degradation and the desertification phenomenon. Also, it should be mentioned that some preliminary measures, specifically, development of land markets, solution of the lands' parceling, and improvement of the Republic's irrigation systems will further improve the land utilization mechanisms.

3.2. FINANCIAL RESOURCES AND MECHANISMS

The types of charges for environmental protection and natural resources use (the revenues from both are included in the State Budget), as well as size of these charges, are regulated by the Law of the Republic of Armenia on environmental and Natural Resource Use Charges, as well as other laws and regulations for the implementation of this law. This law and related laws and regulations have established economic mechanisms for environmental protection, creating equal conditions for users, raising necessary financial means for environmental measures, and controlling activities that have negative impacts on the environment. The following types of pollution control charges are used: – on hazardous substances emissions in the environment (air and water basins); – for industrial and other wastes, according to prescribed norms; and – for environmental damages. The following types of natural resource charges are compulsory: – for water usage; – for underground natural resource extraction; and – for biological resource use. Tax legislation in the sphere of natural resource use and environmental protection was reformed in the period 1997–2000, when new tax laws were adopted, based on international criteria. Connected with these developments, there is an ongoing trend to increase the charges for natural resource use and environmental protection, whose revenues are included in the State Budget of the Republic. The system of environmental charges on non-environmentally certified products has been established in the Republic of Armenia. By the adoption of the Law of Republic of Armenia "On Nature Protection and Nature Use Charges" and by-laws providing the application of this law, it became possible to reduce the negative environmental impact and to achieve more sustainable use of natural resources, as well as to ensure environmental investments and generating of financial resources aimed to increase revenues to the State budget.

There are several shortcomings in this sphere. Over the last years, the state expenses to cover the fight against desertification and consequences of desertification activities made up around 0.4% of the Republic's GDP and payments for environmental protection and utilization of natural resources were 25% of those expenses (EPRA, 2000). The "National Action Plan on Desertification in Armenia" had to estimate demands for financial resources in terms of long-term segments (for 5–10 years) and the measures implemented, based on each year.

The national strategy will become complete if it is supplemented by the financial program including all possible financial sources (state, private and the ones acquired through credits and international cooperation) and the financial mechanisms. Also, it has to be taken into account that economic mechanisms are based mainly on the fees collected from the land, water and natural resources' utilization, and often fees for use of natural resources or tax rates and the ways they are used do not have interconnection with reproduction of these resources.

Besides that, there are no factual sanctions for a damage of natural ecosystems. Specifically the land tax should stimulate a proper land use and create conditions for land reproduction through the resources collected. In realty, according to the acting legislation, the land tax is a source of income for local government authorities (village municipal bodies) and is used mainly to maintain the administrative staff of municipalities and for other expenses. According to the Law on "Land Taxation," collection of taxes for farm lands' surface is 15% and for non-farmlands' surface is 0.5–1% of a net income calculated, based on a cadastral assessment. Practically, the land tax does not have a corresponding economic substantiation and, in terms of its origin, it does not have a specific target. The land tax is paid by land owners, permanent and temporary users of state-owned lands who get sanctions if the taxes are not paid. However, there is no legal responsibility for human-caused land degradations.

Allocation of financial resources for projecting and implementing of action plans against desertification is substantially conditioned by the level of economic development of a given country. Of course, the economic growth registered in our country over the last years, creates the necessary prerequisites for allocation of resources for fights against desertification. The specific weight of agriculture in the Republic's GDP is rather substantial. In 1995 it was 38.7%, in 1998 – 30.8%, in 2000 – 23.1%. Although there is a tangible difference between the GDP and agricultural growth, the role of agriculture and production reprocessing sectors of this branch, especially the food industry is crucial for an overall economic growth. However, at the same time the economic growth of our country is still accompanied by favorable conditions for land degradation and desertification.

3.3. LESSONS LEARNED FROM LAND PRIVATIZATION

In that sense, land privatization had a negative impact. The total land base in Armenia is nearly 3 million ha. Arable land in Armenia (cultivated and perennial crops) totals 550,000–580,000 ha with an additional 800,000–830,000 ha of meadows and pastures. Unused land and forests comprise over 50% of the total land area. Of the arable land, some 320,000 private farmers hold about 460,000 ha with another 115,000 ha held by the state. All pastures, forests and unused land remains under state ownership. The well-documented and successful Armenian farm land privatization program undertaken in the early 1990s resulted in about 1.3 million land parcels and private farm holdings. These parcels generally consist of three to four smaller parcels, totaling an average of 1.3 ha in size (fluctuation is 0.4–4.5 ha). Such a small farms particularly having no modern agricultural equipment, without conducting intensive agriculture (unsatisfactory use of fertilizers, pesticides, and herbicides, breaking of agro-technical rules implementing insufficient agro-scientific technologies) and having chop lands (approximately 1 million) are not able to improve land utilization practices in general. However, individual farms are now reported to average 2.2 ha, indicating some consolidation via land sales and leases (land leases for up to 25 years are now possible) with 15% of farmers reportedly leasing land from village councils. A program of first title registration, with World Bank and EU support, is underway. However, to date, less than one half of 1.3 million first title certificates for the privatized parcels have been issued. Development of a land market is highly dependent on the completion of registration of these land parcels and title issuance. Some fine-tuning of the basic legal framework for land transactions may also be needed to enable development of a vibrant land market. In particular, legal and other constraints that inhibit the willingness of financial institutions to accept land as collateral will need to be removed. At the same time, the consolidation of land into larger operating units than the current average size of Armenian farms is critical to a more productive agricultural sector. Certainly higher yields and increased labor productivity for many crops can be achieved on small plots. However, these levels are far from being reached in Armenia. There are often economies of scale, needs for rotation, and for certain crops, such as cereals, production gains through the use of modern equipment that are only feasible on larger size farms. Whether this occurs through leasing or land purchase is less important than the creation of mechanisms to allow and to facilitate this to take place.

At the same time there is a decrease of rates of arable land use. In 1999–2001 it was 60.8% based on data prepared by specialists of the Ministry of Agriculture. Almost half of the agricultural communities (47%) use 52.6% of arable lands. The rate of reserved arable land utilization is also poor (42%). In general, the total arable area of cultured plants has been reduced in 1991–2000 up to 113,300 ha; in 2001 they have been increased up to 13,900 ha compared to the previous year. However, they have not reached the level of 1991 (417,000 ha) yet (Armenia's Statistical Annual., 2002).

Arable lands comprise 35.5% of total agricultural land surfaces, and their insufficient utilization is a cause for land degradations. Hence, it is crucial to enlarge agricultural farms, as well as to develop and implement legislative, normative and economic mechanisms for increasing their productivity.

3.4. LAND POLLUTION AND DEGRADATION

As it is mentioned in the Report of the RA Minister of Environmental Protection presented at the 5th All-European Ministerial Conference “Environment for Europe,” enterprises of non-ferrous metallurgy and household wastes are sources of land pollution in Armenia. According to some estimation, 51,000 ha of lands are polluted by heavy metals (Ministerial Report, 2003). There are many cases in our urban planning when hotels, trade centers, private houses, garages and other structures are built on the territories of the parks and orchards. Hence, the principles of the main plan of a diverse settling of population are not taken into account, according to which it is necessary to emphasize the importance of having green belts around cities, proper planning of structures polluting environment, banning of constructions on agricultural farmlands, use of inconvenient land slopes for settlements, enlargement of poor developed settlements next to intensively developed ones, increase of territories covered by forests and other measures.

The same is related to mining of natural resources. Privatization of mines has negative influence. Private entrepreneurs may easily and rather inexpensively obtain a patent for new farmlands in order to use them as new mines for exploring mineral resources. As of to 2004, a patent for ore deposits coasted 10 million drams (US$1 = 360 Armenian Drams[1]) and only 500,000 drams and for non-ore deposits. The percentage of environmental expenses was fluctuating only between 1.3–8% with regard to the volume of mined and realized mineral resources. Only 50,000 drams were paid for 1 ha of lands, and here there is no any differentiation for the land fertility. Above mentioned has a negative role for activation of land desertification.

Mines should be created mostly on land non-useable for agricultural purposes. Fees for patents and exploitation of natural resources should be determined in the way that it would be more profitable for entrepreneurs to exploit old (existing) mines rather than obtain new ones. It is necessary to conduct special economic investigations, particularly pricing of land recourses, to find out the losses of our country’s profit in case of providing fertile farmlands for mining. Moreover, fertile farmlands (arable lands) should be provided for mining only

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[1] in 2007.

in exceptional cases and if the mineral resources mined bring more profit compared to the agricultural use of a given farmland.

There is a wide variety of measures projected at the "National Action Plan on Desertification in Armenia" aimed to improve land use, to implement a beneficial urban planning, industrial, transport, and energy technologies fighting desertification, as well as directed to an efficient use of the Earth entrails and water resources, however, these measures contain the following shortcomings:

- There are no clearly defined financial mechanisms and responsible authorities for implementation of the above-defined measures.
- Suggested measures for improving mechanisms of environmental economics are of a general character and do not include leverages for economic stimulation or sanctions which would influence the efficient utilization of natural resources and environmental protection.
- There are no proper justifications and recommendations for developing those directions of forestry that are crucial for preventing desertification.

According to the forecast, 4–6% should be allocated from the Republic's budget for these purposes (in 2000 this index was 2%) and 2% of GDP which would correspond to the developed countries' indexes.

4. Research Activities: Gaps and Solutions

In Armenia some research is conducted through the state financing, which is more or less related to the issues of environmental protection, utilization of natural resources, and agriculture. Today's research activities in Armenia almost totally is overlook on the problems around desertification, while it is very important to develop and propose suggestions, calculations, and justifications with regard to this problem. This research should be directed to prevent and mitigate the desertification outcomes and even their further elimination. Scientific justifications should have a proper basis for increasing budget allocations for the environmental protection and anti-desertification activities. The research topics are as follows:

- Institute of Economics, National Academy of Science's: "Basic Problems of Establishing and Improving Agrarian Markets in the Republic of Armenia," "Basic problems of Employment in the Agricultural Sector," "Environmental – Economic Problems of Developing the RA Industry, Agriculture, and Transportation"
- Institute of Economic Research of the Ministry of Finance and Economics: "Basic Problems of Environmental Protection and Utilization of Natural Resources"

- Armenian State University of Economics: “Ways to Improve Methods of Ecological Assessment of Economic Activities”
- Six research topics are directly related to the agricultural sector and are developed at the Research institute of Agriculture (under the jurisdiction of the Ministry of Agriculture): “Ways to Improve Food Processing Safety in the Republic of Armenia,” “Necessity, Prerequisites, and Mechanisms to Form Cooperation in the Republic’s Agro System,” “Environmental Economics Problems of Utilization of Natural and Productive Resources in the Armenian Agricultural Sector,” “Increasing Efficiency of Privatized Farmlands’ Utilization,” “Ways to Increase Efficiency of Human Resources and Labor Productivity in the Republic’s Villages,” “Urgent Economic Problems Related to the Intensive Development of Agricultural Productivity in the Period of Transition”

It is apparent from the above-mentioned research topics that none of them is directly related to economic problems of fighting against desertification; in many cases pure methodological questions are discussed. The research related to exploitation of natural resources and desertification should be mainly concentrated at the Research Institute of Agricultural Economics of the Ministry of Agriculture RA, but the Institute has no sufficient recourses. There are only 39 researchers at the Institute. The following research topic may be offered as a state order for this Institute: “Economic-Environmental Problems of Land Resources Utilization” which will include research of economic problems of land utilization and anti-desertification.

It is also appropriate to conduct a research on desertification at the Institute of Economics of the National Academy of Science and at the Institute of Economic Research of the Ministry of Finances and Economics. The research should be ordered by the RA Government. However, a private financing of research activities may also have a crucial role in solution of this problem.

At the same time, it should be emphasized that there is a need in reforms at these Institutes, particularly preparation and involvement of young scientists. These reforms are possible only through a sustainable and substantial financing from the state and international sources, including grants. Only Armenian State University of Economics has started to prepare specialists of environmental economics but the future experts do not get enough knowledge regarding the problems of desertification and their prevention. In that sense, it is important to develop study programs and curriculum, which will make possible to prepare anti-desertification specialists. The same type of experts should be prepared also at the Academy of Agriculture. Besides that, it is very important to realize re-training activities. Also, preparation of school-teachers of this sphere must be organized in Armenia.

It is necessary to establish public awareness services which will periodically inform our population about basic problems of desertification, activities against this phenomenon, and measures taken. The overall alarming situation with desertification and ways to further prevent them should be periodically discussed through the mass media sources, including press, TV, and radio and Internet.

Fighting against desertification is not a case for a separate country and international cooperation in this area is a necessary activity towards solution. Armenia needs experience, and investigation of case studies about desertification in developed countries. It is also important to involve specialized international organizations and their financing, especially the European organizations, taking into account their principles of safety and sustainability. The anti-desertification problem is also important in terms of purposefulness of Armenia's possible integration into the European Union. Grants for anti-desertification activities obtained from various international organizations could provide shifts.

The "National Action Plan on Desertification in Armenia" does not take into account the fact that Armenia is WTO member-country, while it is important to conduct analysis and evaluation of survival and environmental protection issues, including desertification through the membership into this organization and measures taken. Substitution of VAT in agriculture with the state subsidies (up to 2009) may lead to a drastic increase of desertification processes. The increasing volumes of agricultural products and solving the problems of exporting the republic's agricultural products should take into account the efficient utilization of land resources. The Government of our Republic (including a special subunit dealing with WTO under the jurisdiction of the Ministry of Trade and Economic Development) has to raise successively the issues related to environmental protection, including the ones appearing from the issues of fighting against desertification. This aspect is clearly stated in the Doha Declaration. According to this document, WTO is responsible for provision of a necessary technical assistance in order to solve the problems related to survival and environmental protection. According to the above mentioned Ministry of Trade and Economic Development and its External Economic Relations subunits, as well as the Ministry of Foreign Affairs and its Department of Economics should have a very important role in the issues of international cooperation to solve the problem of desertification.

5. Conclusions

A certain shifts in secure and sustainable policymaking took place in Armenia, new forms of activities appeared, rich set of legislative documents were adopted, new administrative and working bodies were established, the scope of the international cooperation became broader and its new forms appeared. In this connection, further analysis and new recommendations for the future would be valuable.

Financial and economic institutions in environmental policy making are on the first stage of development. The system of economic instruments has been designed and its application in the fiscal area proved to be very efficient and contributed to the considerable growth of the revenues to the income part of the State budget. The problems in this field permanently are in the focus. Setting up system of pricing of land, water and other environmental resources, which necessary tool for natural resource management, is an important problem not only for Armenia.

Much of secure development issues arise from inefficient land administration poorly defined institutional responsibilities and limited enforcement. Little scientific basis exists for the current land use planning. Obtaining accurate data is one of the main problems for environmental analysis in Armenia. This is the basis of successful solutions. It is important to investigate above described problems on the regional level (involving Armenia, Georgia, and Azerbaijan) and to speak about sustainable solutions not only for one country but for the region as well. Effective solutions could be possible only thru implementation of complex measures and integrated strategies.

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USING A DECISION SUPPORT SOFTWARE IN THE COURSE OF THE PLANNING OF A WASTE MANAGEMENT SYSTEM IN HUNGARY

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Abstract. Modernizing and rearrange the waste management system to the norms of the European Union is one of the most important tasks of the environmental protection in Hungary. Connected to this the Middle-Danube Region Waste Management System is one of the biggest infrastructure investments at present. This investment having an effect on six counties could solve the waste treatment problems of the residents for at least 20 years in the settlements affected. Systems approach mind is needed to complex waste management systems like this, in which beside landfills, plants for separated collection as sorting devices, compost piles, transfer points, waste yards are included and the recultivation of the inconvenient landfills is needed, too. Meeting the systems approach mind is possible only with computational decision support tools. Parmenides EIDOS is a module-based decision support software, specially developed for the economy and the corporate management. The goal of the research was to adapt these software toolkits to environmental field and to examine how the software could be used in the course of the planning of the Middle-Danube Region Waste Management System. According to the authors experience some modules of the software are able to apply well to simplify the complex decision situation and to lay stress on the most important problems. Subjectivity is unavoidable of course, but the subjective elements aid rather than hinder the process due to the group decision-making technique. (Wilkins, 2003) Further advantage is that the data, results are presented visually by this means the time of understanding decreases and keeping in mind become easier than reading naked data or tables. That is why the figures made with EIDOS

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could be part of a marketing material prepared for the population to increase their support for the investment.

Keywords: computer-aided visualization, decision support, environmental impact assessment, waste management

1. Introduction

The membership of Hungary in the European Union means obligation and at the same time possibility to join up in the respect of environmental protection, since the Union provides financial sources for environmental improvements. The current environmental policy of the EU is based upon the concept of Sustainable Development. In the environmental sphere, Sustainable Development is understood as an interdependent relationship between the economy, infrastructure, settlement and the way of living, taking into consideration the bearing capacity of the environment and natural resources (Eisner et al., 2007).

Modernizing and rearrange the waste management to the norms of the European Union is one of the most important tasks of the environmental protection. The aim is to expand a comprehensive, up-to-date waste management structure that is to harmonize and widen the available and planned waste treatment plants and capacities and to establish new, regional waste management systems, which cover the whole country. A waste management system is defined as a set of elements (objects, processes) linked by relationships (Gaska et al., 2007).

The Middle-Danube Region Waste Management System set the aim to handle the municipal waste of 680,000 people of 170 settlements affected (Figure 1) which includes the creation of the technological, constitutional and the communication conditions. The system contains the treatment of the waste coming from the households, the economy and from the institutions covering the separated waste collection as well. Though public services are developed in the whole of the planning area, the waste elimination is done solely by deposition at present with negligible treatment. That is why the main aim is to produce secondary raw materials from paper, glass, plastic and metal, to compost and to collect the hazardous material separately in accordance with the Best Available Technology. By this the needed landfill capacity and territorial demand could be decreased therefore the environmental load caused by the landfills would be mitigated. Further aim is to improve the environmental consciousness of the inhabitants for the success of the project.

The Environmental Impact Assessment (EIA) is a prediction method that aims to predict and estimate the expected and essential changed conditions of the environment due to pre-arranged human activity and through this to influence decision-making (Rédey et al., 2004). By the valid Hungarian legislation constructing waste disposal plants is liable for environmental impact assessment. The aim of the environmental impact statement is to inform the decision makers and the general public about all detailed information of the planned activity and it's alternatives either, to avoid or moderate the coming negative effects would be possible (Felleman et al., 2006).

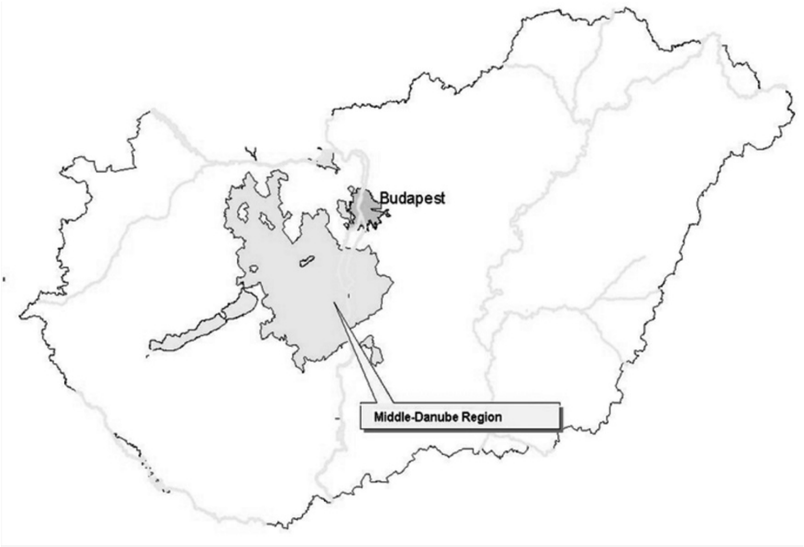
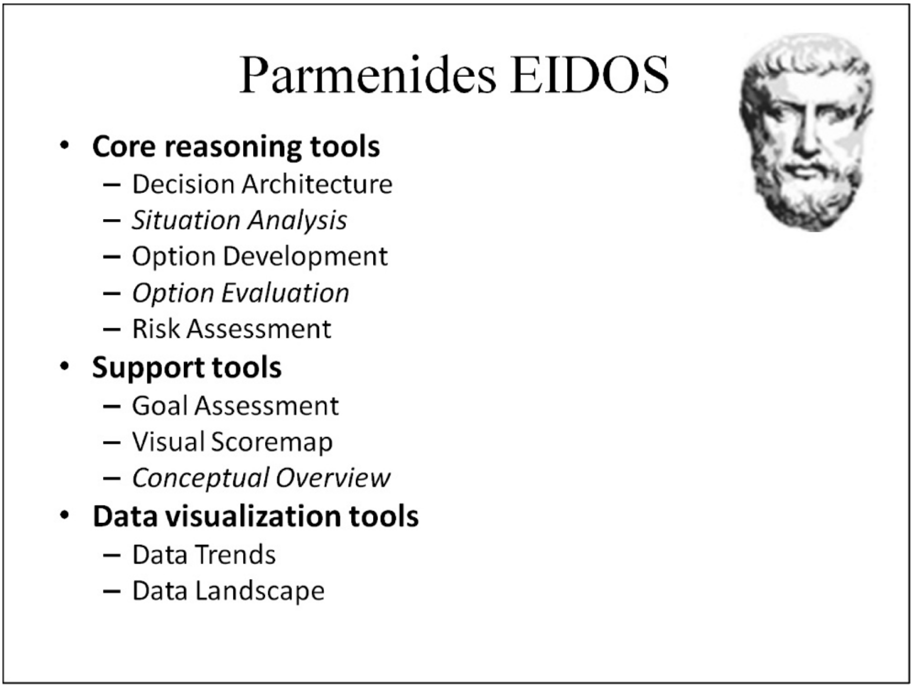


Figure 1. The regional extension of the Middle-Danube Region Waste Management System.

2. Materials and Methods

Decision Support Systems Decision Support Systems (DSS) are defined as computerized systems, which include models and databases and they are used in decision-making. These tools help in the procedure of decision-making and in choosing the best (economic, social or environmental) alternative solution (Manos et al., 2007).

Parmenides EIDOS is a decision support software, specially developed for the economy and the corporate management. It comprises ten modules, which make up a whole decision cycle and by the visualization techniques could help the decision making process in different fields. There are five core reasoning tools, three support tools and two data visualization tools (Figure 2). These



Parmenides EIDOS

- **Core reasoning tools**
  - Decision Architecture
  - *Situation Analysis*
  - Option Development
  - *Option Evaluation*
  - Risk Assessment
- **Support tools**
  - Goal Assessment
  - Visual Scoremap
  - *Conceptual Overview*
- **Data visualization tools**
  - Data Trends
  - Data Landscape

Figure 2. The modules of the software parmenides eidos.

provide an innovative approach to managing the entire decision making process by visualizing complex situations, by helping to reconcile different positions of different decision makers, and supporting the identification of possible courses of action. It also assist in analyzing proposed solutions against established metrics and developing implementation plans. (Parmenides EIDOS 6.5.6 (http://okoret.uni-pannon.hu)) Primarily a new way of thinking is opened by it. The software uses the group decision making technique, beside which the scientific literature lines many reasons up.

One of its advantages is the incitement, since working in a group encourages greater achievement. The complete group has more information than either of its members alone. The members of the group can learn from each other, with which could improve the performance, too. In groups the evaluation becomes more objective and the creativity develops since the members possess different background knowledge, so they can put to use the information in other way. (Sramó, 1996).

The authors used the toolkits of EIDOS to get experiences about its usefulness in the process of the waste management system planning. The work was built on the method of brainstorming leaning on the earlier studies about the waste management condition of the region and taking into consideration the legal requirements of course.

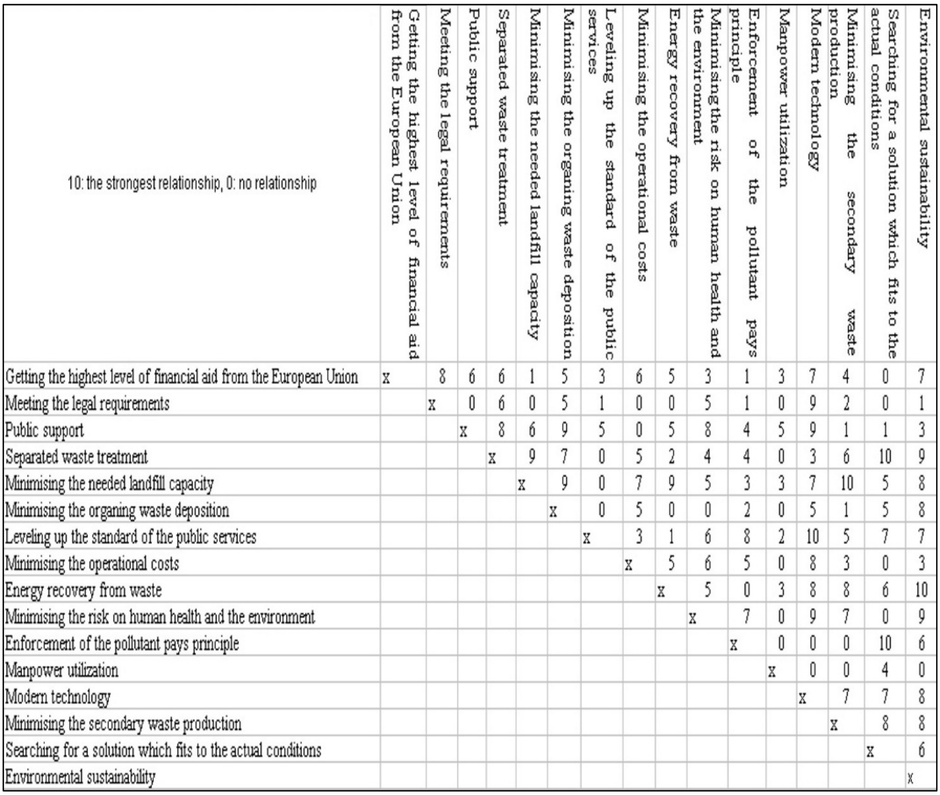
3. Results

Some of the tools of the software seemed to be useful in the process of the waste management system planning, but not all of them are suitable in this case. Three of them are presented in this paper.

3.1 THE MODULE "CONCEPTUAL OVERVIEW"

The module "Conceptual Overview" is a tool of the software built on the group-technique, which can be used to map complex, multidimensional relationships between project components in a 3D space. Sixteen factors were collected seen in Table 1, which are important in terms of the examined project.

TABLE 1. The collected factors that are important in the process.



10: the strongest relationship, 0: no relationship	Getting the highest level of financial aid from the European Union	Meeting the legal requirements	Public support	Separated waste treatment	Minimising the needed landfill capacity	Minimising the organing waste deposition	Leveling up the standard of the public services	Minimising the operational costs	Energy recovery from waste	Minimising the risk on human health and the environment	Enforcement of the pollutant pays principle	Manpower utilization	Modern technology	Minimising the secondary waste production	Searching for a solution which fits to the actual conditions	Environmental sustainability
Getting the highest level of financial aid from the European Union	x	8	6	6	1	5	3	6	5	3	1	3	7	4	0	7
Meeting the legal requirements		x	0	6	0	5	1	0	0	5	1	0	9	2	0	1
Public support			x	8	6	9	5	0	5	8	4	5	9	1	1	3
Separated waste treatment				x	9	7	0	5	2	4	4	0	3	6	10	9
Minimising the needed landfill capacity					x	9	0	7	9	5	3	3	7	10	5	8
Minimising the organing waste deposition						x	0	5	0	0	2	0	5	1	5	8
Leveling up the standard of the public services							x	3	1	6	8	2	10	5	7	7
Minimising the operational costs								x	5	6	5	0	8	3	0	3
Energy recovery from waste									x	5	0	3	8	8	6	10
Minimising the risk on human health and the environment										x	7	0	9	7	0	9
Enforcement of the pollutant pays principle											x	0	0	0	10	6
Manpower utilization												x	0	0	4	0
Modern technology													x	7	7	8
Minimising the secondary waste production														x	8	8
Searching for a solution which fits to the actual conditions															x	6
Environmental sustainability																x

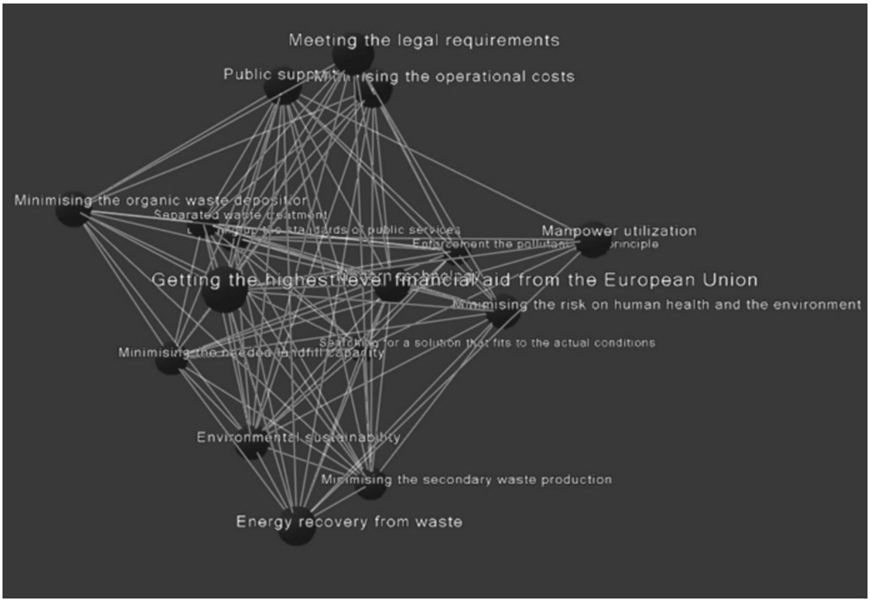


Figure 3. The tension structuring molecule with the module "Conceptual Overview".

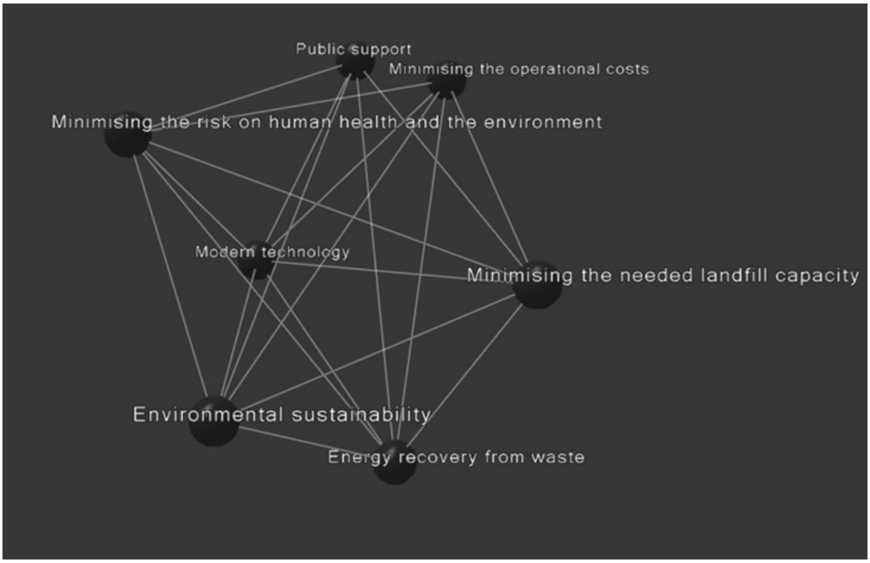


Figure 4. The simplified decision situation.

After defining the factors the relationships were rated between each pair of them by a value from zero to ten. The values can be seen in the table are averages. Negative values were not added, because there were no factors that have a meaning contrary to each other. As a result, the model shows the relationships in a tension-structuring molecule (Figure 3), with the placement of the elements based on the combined calculation of all relationships, so it evaluates the synergies and tensions among them. Those elements which stick out from the model were removed thus the decision situation would be much simpler (Figure 4). With the model, the most important fields of the problem brought up can be found easier. After that these can be taken into other modules for further analysis. In this case, these are the public support, the operational costs, the risk on the human health and the environment, the modern technology, the landfill capacity minimizing, the energy recovery and the sustainability. These are the main goals, the central criteria of the project that need to be performed in the waste management system.

3.1. THE MODULE “SITUATION ANALYSIS”

The “Situation Analysis” tool helps to reveal the nature of a problem. In Figure 5, the situation analysis chart is shown with the barriers and driving forces of the project. These factors are linked with arrows to define the relationships between them. Green arrows show increasing impacts that means relationships that reinforce the target factor. Red arrows indicate decreasing impacts also relationships that counterbalance or mitigate the target factor. Arrow thickness refers to the strength of the impact. Though all factors in the “Situation Analysis” are important to the problem, some of them are likely to be more relevant for further analysis than others. Using the “Active/Passive Map” generated to the chart, key factors are easier to be identified (Figure 6). All of them are represented by a numbered ball in compliance with the chart. These positions are determined by the inputs and outputs of the components. Looking at the figure it becomes unambiguous, which are the key-problems, where effects have to be moderated. In the “Active/Passive Map”, factors at the top such marketing are active, they drive other factors. Any actions one takes regarding the active factor will have a ripple effect on the others. Factors to the right are passive, they are driven by other factors and are therefore likely to be outcomes or goals, such as public support or the financing in this case. Key factors tend to be both active and passive and are placed especially the upper right section.

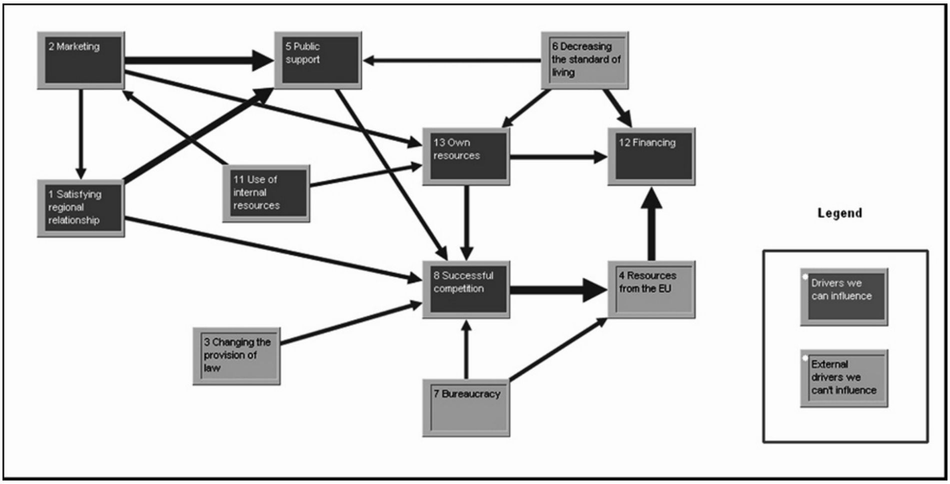


Figure 5. “Situation Analysis” chart.

These have the strongest links to the other factors; changes in those factors will have the most influence on the other barriers and driving forces of the problem. Therefore, concentrating attention on these key factors will have the most significant impact on the project. In this case, the successful competition and the satisfying regional relationship need to be marked as the most important factors since without them the project would not be developed at all. Without successful marketing the regional relationships cannot be improved and the public support would not be reached sufficiently. That is why it is needed to lay much more stress on it than earlier.

3.2. THE MODULE “OPTION EVALUATION”

The most important fields of the group decision making are the methods in connected to generating ideas, systematization, analysis for example brainstorming and classification. Those methods are also important, with which the different versions can be evaluated on the strength of several viewpoints simultaneously (Cserny, 2000). The “Option Evaluation” module of the software Parmenides EIDOS provides an opportunity to this. Effort to evaluate

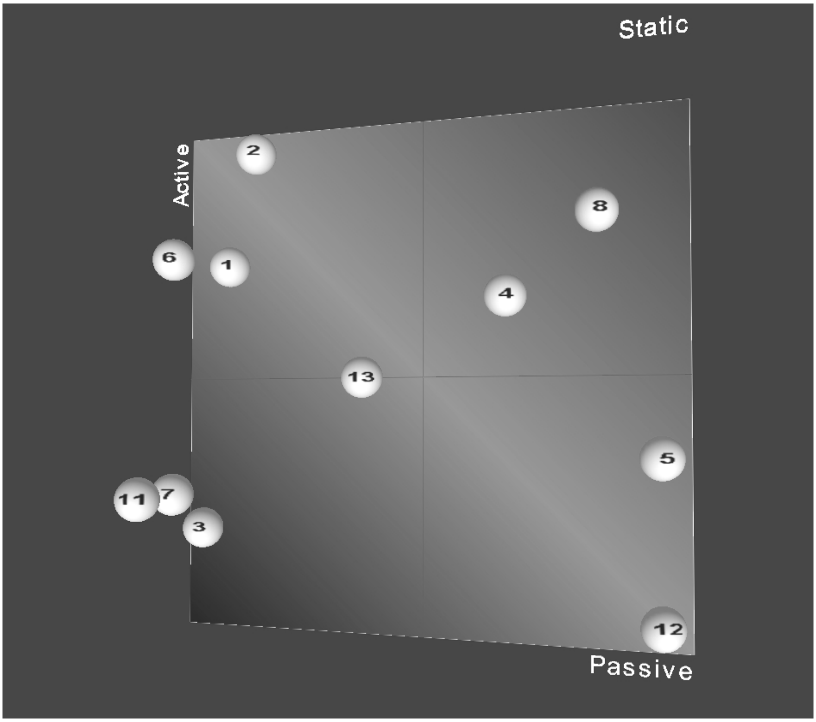
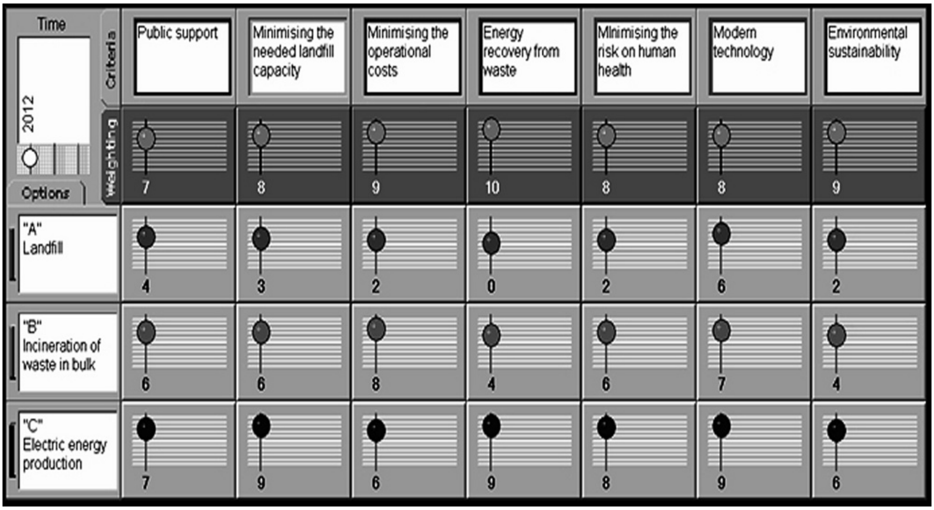


Figure 6. Active/Passive Map.

the alternatives with numbers is a general tendency in the computer-aided decision-making systems. This module evaluates options according to weighted criteria in multiple views and then makes a comparison among the options. By affecting the choice among the options created by generating rankings from the evaluation, it supports an improved decision-making. Three technological alternatives were examined by the developers of the environmental impact study of the Middle-Danube Region Waste Management System to manage the problems in regional level. The alternatives differ from each other in the treatment technology referring to the municipal waste that constitutes the biggest part of the produced quantity. Mechanical-biological pre-treatment then fractionating are the central elements in version “A”. The fine fraction would be used for recultivation; the rough fraction would be deposited in landfills. The municipal waste would be transported directly to incinerator, where waste heat utilization would be possible in case of realizing version “B”. While in version “C”, fuel material with high heating value would be turned out from the rough fraction received from the fractionating after the mechanical-biological pre-treatment. This fuel material would be used for electric energy production (Figure 9). The rate of municipal waste recycling in many countries throughout Europe is minimal. Waste incineration mainly helps to reduce the quantity of waste to be landfilled, make the remaining slag more stable than untreated waste, and obtain energy from the incineration. This is why the waste incineration is more environmentally friendly than waste landfilling. (Kikuchi et al., 2008).



	Public support	Minimising the needed landfill capacity	Minimising the operational costs	Energy recovery from waste	Minimising the risk on human health	Modern technology	Environmental sustainability
Weighting	7	8	9	10	8	8	9
"A" Landfill	4	3	2	0	2	6	2
"B" Incineration of waste in bulk	6	6	8	4	6	7	4
"C" Electric energy production	7	9	6	9	8	9	6

Figure 7. The evaluation of the alternatives.

The technology of treating the smaller waste fractions is the same within the scope of the three alternatives due to their characteristics and the legal requirements. By the reason of these, the green waste would be chipped and classified before recycling and the separate collection of the hazardous waste would be solved, too. (Diószegi, 2008) In Figure 7, the evaluation of the alternatives is visible. The criteria are the goals defined with the “Conceptual Overview” and are weighted according to the members’ opinion on importance of the goals in 2012, the year by when the investment should have been fully developed. The weighting values are from 1 to 10. There are no negative values of course, because all the criteria are important and have to be weighted with high values. The three technological alternatives are defined as options in the matrix and rated with a value from –10 to 10 according to each goal. The analysis charts based on the entered data into the matrix present a ranking among the alternatives. These diagrams support the experts' arguments for version "C". The overall technological flow-chart of the planned waste management system can be seen in Figure 8.

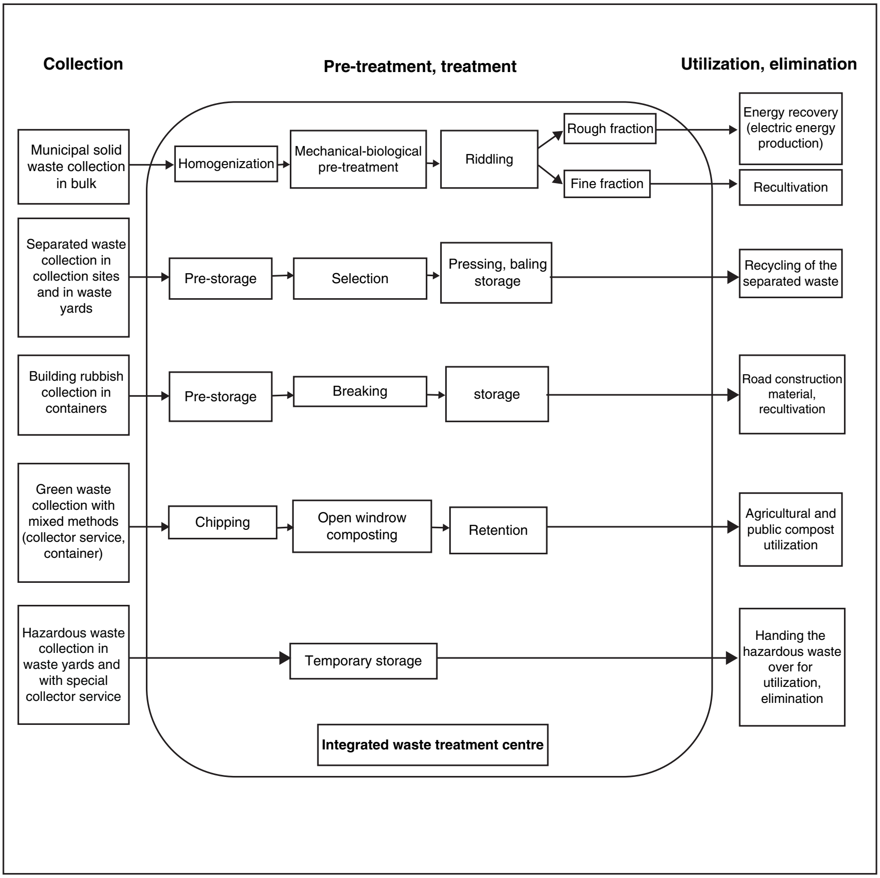


Figure 8. The overall technological flow-chart of the planned waste management system. (From Diószegi, 2008.)

The examined software is not able to appoint the gathering headquarters of the zones. It was carried out with cluster-analysis and it does not form the part of this paper.

4. Expectable Effects in Case of the Realization of the Project

The waste management developments produce many indirect social and environmental benefits as a consequence. The most important social benefit is the job generation during both of the construction and operation phases of the investment. Many fields which are repulsive with a view to tourism can be eliminated due to the recultivation. And by this the attraction of the region increases. In case of realizing this project the condition of the environmental elements having special regard on the soil and the underground water can be improved. The investment has solely small-scale local negative effects (land use, minimal hazardous material emission and hazardous waste deposition) using the planned technologies. The positive effects of the project can be explained by the decreasing quantity of the deposited waste and by the novel technological, production and employment conditions in the region. Thus the project is definitely reasonable towards the development of the whole region (Diószegi, 2008).

5. Conclusion

Modernizing and rearrange the waste management is one of the most important tasks of the environmental protection in Hungary. The Middle-Danube Region Waste Management System is one of the biggest environmental infrastructures in the country, which set to aim to set the aim to handle the municipal waste of 680,000 people of 170 settlements affected. Systems approach mind is needed to manage a complex system like this, which is possible only with computational decision support tools. Some of the modules of the software Parmenides EIDOS are presented in this paper which appeared to be useful to support the decision-making connected to Middle-Danube Region Waste Management System procedure. The “Conceptual Overview” tool can be used successfully in the beginning of the process to get a clear overview about the main goals which should lead the decision makers during the implementation planning. The “Situation Analysis” shed light upon the importance of the marketing. It is important particularly in the case of the incinerator that has put up a significant resistance among the population. To convince the population of the necessity of the incinerator and the waste management system in general the “Option Evaluation” tool could be really advantageous due to the expressive visualization.

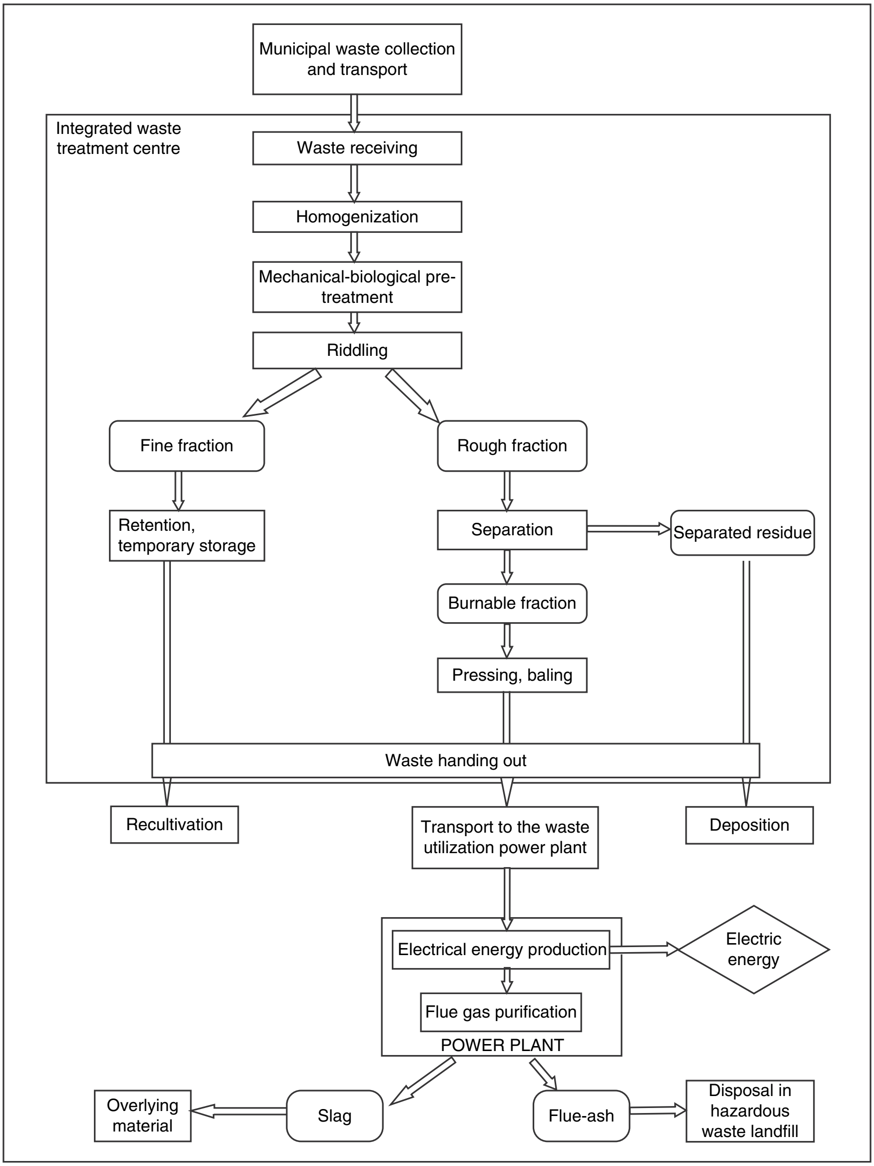


Figure 9. Technological flow-chart of the municipal solid waste treatment. (From Diószegi, 2008.)

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EXAMINATION OF CONDITION OF SMALL STREAMS AND RESULTS DISPLAYING IN ENVIRONMENTAL INFORMATION SYSTEM

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Abstract. The society has been playing more and more significant role in EU's and Hungary's environmental policy considering that environmental consciousness of the people raised increasing demand on environmental information. The bottleneck of this process is the lack of public information on environmental data. Therefore it is essential that the residents of small regions may easily access information on the state of their narrower environment and have the possibility to take part in the decision process. The Institute of Environmental Engineering, University of Pannonia has undertaken this challenge and developed an online environmental information system. This system is able to receive and process the collected environmental data via Internet. These data on the environmental elements (air, surface water, noise) are then available to the public as a web service displayed by GIS and graphical tools. The system had to meet simplicity and comprehensibility. The database can be efficiently used in areas where displaying spatial information on maps is important. Aim of the project to define physical and chemical parameters of surface waters and apply Water Framework Directive (WFD) for examined water bodies further goal is to display results via internet in Environmental Information System developed by its authors. As the load to our surface water became greater, it created increasing demand for adequate quality and quantity waters. A good condition is available with prevention of the quality ruin and provides sustainable water manage ment. The Water Framework Directive (WFD) was created as the long-term water policy of the European Union. Member States have required achieve good ecological and chemical status in all bodies of surface water by 2015.

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Measurements and water sampling were taken at the examined streams. Streams were categorized according to typology. The field measurement (temperature, pH, conductivity, chlorophyll-a, PAH) and laboratory texts (COD_t, PO_4^{3-}, NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}, Na^+, Ca^{2+}, Mg^{2+}, K^+, Si^{4+} Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}) has been taken. Measured results have been compared with MSZ 12749 standards and accordingly streams were classified. Bedrock has taken effect via main ions of the water so this element of the typology has been proved by main ions. According to results of the examined water the followings were determined: nitrate, nitrite and phosphate-ion from the gardens, agriculture areas and sewage significantly pollute the surface water. Traffic means further pollution, in this case organic compounds or heavy metals can solve out to the water. On the homepage bar charts show measured values at different sampling sites of the streams. On the Google Map distances between two sampling sites were coloured according to water quality colour scale. These provide generic information about condition of watercourse comprehensible for everyone.

Keywords: watercourses, water quality, water framework directive, GIS, visualization

1. Introduction

Society has been playing more and more significant role in EU's and Hungary's environmental policy considering that the environmental consciousness of the people has raised increasing demand for environmental information. Therefore it is essential that the residents of small regions may easily access information on the state of their narrower environment and have the possibility to take part in the decision process.

It is very important to investigate surface water. As the load to our surface water become greater, it created increasing demand for adequate quality and quantity waters. A good condition is available with prevention of the quality ruin and provides sustainable water management. The WFD (2000/60/EC) was created as a long-term water policy of the European Union. Member States are required to achieve good ecological and chemical status in all bodies of surface water by 2015 (Directive, 2000/60/EC). It provides a framework for Member States and to be applied taking into consideration local features. Comparing this new system with the existing system the basic difference is that WFD is able to provide information about condition of water bodies entirely and not only about sampling sites. Working out of the River Basin Management Plans by 2009 is demanded by WFD and national laws.

Currently the most important issue of WFD is to establish a well-prepared monitoring system in Hungary. In Hungary this means a three stage monitoring system (surveillance-, operational-, investigate) according to WFD rules. Surveillance monitoring aims at assessing long term changes in natural conditions resulting from human activity. Operational monitoring is to be carried out as an additional measure for water bodies that are at risk of failing to meet the Directive's environmental objective. Investigative monitoring is to be only carried out in individual cases, e.g. where the environmental standards are not met due to unknown reasons with the aim of determining the causes of such failure (Thomas et al., 2005).

The basis of implementing the WFD is the elaboration of the typology of water bodies. The aims of typology: identification of water bodies, definition of reference conditions and biological monitoring. Hungarian typology based on four parameters altitude, geology, structure and substrate of bed material and size of the catchment area. Twenty-two different types are distinguished in Hungary (1 – High altitude siliceous small streams with coarse bed material; 2 – High altitude siliceous medium-sized streams with coarse bed material; 3 – High altitude calcareous small streams with coarse bed material; 4 – High altitude calcareous medium-sized streams with coarse bed material; 5 – Mid-altitude calcareous small streams with coarse bed material; 6 – Mid-altitude calcareous medium-sized streams with coarse bed material; 7 – Mid-altitude calcareous large rivers with coarse bed material; 8 – Mid-altitude calcareous very large rivers with coarse bed material; 9 – Mid-altitude calcareous small streams with moderately fine bed material; 10 – Mid-altitude calcareous medium-sized streams with moderately fine bed material; 11 – Mid-altitude calcareous large rivers with moderately fine bed material; 12 – Lowland calcareous small streams with coarse bed material; 13 – Lowland calcareous medium-sized streams with coarse bed material; 14 – Lowland calcareous large rivers with coarse bed material; 15 – Lowland calcareous very large rivers with coarse bed material; 16 – Lowland calcareous small streams with moderately fine bed material; 17 – Lowland calcareous small streams with small decline and moderately fine bed material; 18 – Lowland calcareous small medium-sized streams with moderately fine bed material; 19 – Lowland calcareous large rivers with moderately fine bed material; 20 – Lowland calcareous very large rivers with moderately fine bed material; 21 – Turbary, organic featured small streams; 22 – Turbary, organic featured rivers) (Somlyódy and Szilágyi, 2004).

The Institute of Environmental Engineering, University of Pannonia has undertaken the challenge and to develop an online environmental information system. This system is able to receive and process the collected environmental data via Internet. These data on the environmental elements (air, surface water, noise) are then available to the public as a web service displayed by GIS and graphical tool. The system had to meet simplicity and comprehensibility standards. The database can be efficiently used in areas where displaying spatial information on maps is important.

Aim of the project to define physical and chemical parameters of surface water and to support the hydro-geochemical elements of the typology with the analysis of the main ions and to the streams for pollution and apply WFD for examined water bodies further goal is to display results via internet in Environmental Information System developed by its authors. Measured results have been compared to MSZ 12749 standards and based on these measurements streams got classified. The bedrock has its effects through the main ions of the water thus typology had been proved by main ions. According to results of the examined water the followings were determined: nitrate, nitrite and phosphate-ion from the gardens, cultivated lands and sewage significantly pollute the surface water. Traffic means further pollution, in this case organic compounds or heavy metals can solve into the water. Since after processing, these data would be available to the public as a web service displayed by GIS and graphical tool.

2. Material and Methods

One part of this project was to examine physical and chemical parameters of surface water in accordance with the WFD. The following streams were examined (Figure 1) Csenkő (1), Tolcsva (2), Hór (3), Eger (4), Csörgő (5), Cuha (6), Torna (7), Séd in Veszprém (8), Kösély (9), Tócó (10). Examined streams were categorized according to typology. Table 1 presents typological standards of the examined streams.

TABLE 1. Typological types of the streams.

Type	Streams
1	Csenkő, Tolcsva, Csörgő
3	Eger, Hór, Torna, Cuha, Séd
4	Torna
5	Hór,
6	Eger, Torna
12	Hór
16	Tócó
17	Tócó
18	Eger, Kösély

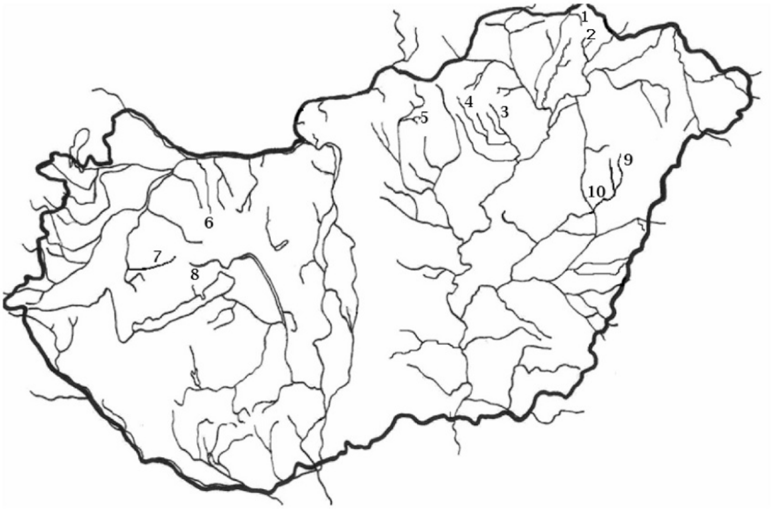


Figure 1. Sampling sites (–).

The system has been split into three significant areas (Figure 2).

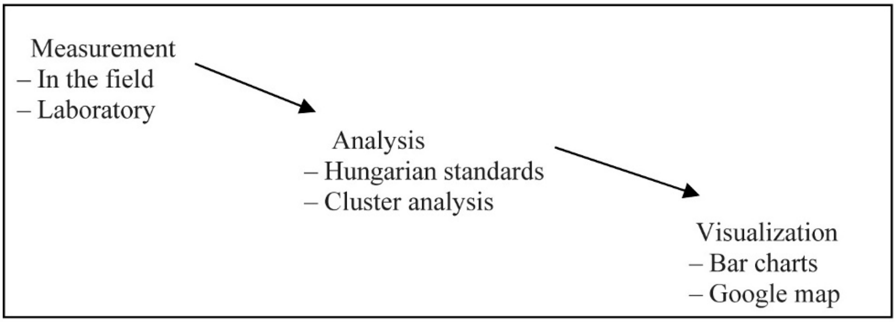


Figure 2. Three stages of the system.

Calibrated and portable Consort C535 was used to take outside measurement. Temperature, pH-value and conductivity were measured in the field. These devices can provide multifunctional water quality monitoring system. UV-fluorescents and spectrophotometer sensors (Figure 3) is able to give information directly about chlorophyll-a, PAH, COD_t and nitrate concentrations in the surface water (rivers, lakes). Application of special software is necessary for the measurements as well as evaluation.

Figure 3. Sensors used.

Sensors can help monitoring of surface water as there is the possibility to receive information directly that can speed up the process of interference. The WFD determines the most urgent needs for new and low cost monitoring devices because all water have to be tested and monitored (Thomas et al., 2005). The eight main ions and N and P forms were analyzed by titrimetry (COD_t, HCO_3^-, CO_3^{2-}, SO_4^2 (Daniel and Pote, 2000) and Cl^- (Incédy, 1981) by spectrophotometry PO_4^{3-}, NH_4^+ (Németh, 1998) NO_3^- (Marczenko, 1976), NO_2^-, by AAS (Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Pb^{2+}) by ICP-OES Na^+, K^+, Ca^{2+}, Si^{4+}, Mg^{2+}).

For estimation of the results SYNTAX 2000 (Podani, 2000) program package was used. The results were displayed in Environmental Information System developed by Institute Environmental Engineering. The homepage created for the project runs under Windows 2003 operation system, but all of its components are platform independent and free to use.

Components:

Database: Oracle Database 10g Express Edition (http://www.oracle.com/technology/products/database/xe/index.html)

Webserver: Apache/Tomcat/5.5.17 (http://tomcat.apache.org/)

MapScript and GIS data: Google Maps Api (http://www.google.com/apis/maps/)

Own GIS data: ArcView 3.2: (http://www.esri.com/software/arcview/)

2.1. RELATIONSHIP OF WFD AND HUNGARIAN STANDARDS

The aim of WFD is to introduce and evaluate current state of water bodies. Verifying good condition and judging distance from the good condition and specifying the causes of risks are main aspects. The water states have to been compared with the so called reference condition (undisturbed state). In the case of reference values WFD prefer criteria system based on flora and fauna rather than chemical parameters. Chemical parameters are still very important in practise, currently they are used to determine the pollution of surface water bodies and for solving the problems occurred. The objective of the WFD is to achieve “Good state” in all European water bodies which is the second stage on the ecological quality scale. Therefore definitions of good and medium conditions are important and the subjects of several research programs (Simonffy, 2001).

MSZ 12749 Hungarian standards (Table 2) were applied in current project. So far on the base of the results of field and laboratory measurements surface water has been qualified according to MSZ 12749 standards in the Environmental Information System.

TABLE 2. Water quality categories (Hungarian standard methods).

A	Oxygen budget (COD_t, *dissolved oxygen*)
B	Nutrient budget (PO_4^{3-}, NH_4^+, NO_3^-, NO_2^- , *chlorophyll-a*)
C	Microbiology parameters (*not measured*)
D	Micro pollutant (Cd^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+})
E	Other parameters (Na^+, Ca^{2+}, Mg^{2+}, K^+, *pH-value, temperature, conductivity*)

Table 3 represents colour scale for water qualification.

TABLE 3. Colour scale for water qualification.

Blue	I.	Excellent
Green	II.	Good
Yellow	III.	Tolerable
Red	IV.	Polluted
Black	V.	Extremely polluted

Due to classification always the worse values are chosen and colours are selected accordingly. According to WFD the I. and II. water quality classes are considered as non hazardous (signed blue colour), III. water quality class is considered as low risk, IV. and V. water quality class is considered as being high risk in case of certain components (signed red colour). Causes of assumptions of risks are signed with different colours in the WFD. Red colour (sewage loading), green (diffuse loading), orange (both) and grey (border). In the future surface water will be categorized according to principle of WFD. Further measurements are needed to specify the limit value and features of the ecological state. Not only the chemical water classification is important but also the ecological water classification based on biological indicator groups (phytoplankton, phytobenthos (diatoms), aquatic macrophytes, macroinvertebrates and fish). The framework has distinguished five ecological status categories (high, good, moderate, poor and bad) (Directive, 2000/60/EK).

3. Results and Conclusion

The choice fell on Oracle database because of the support and experience provided by its company. This version is free to use, and it will allow us the easy switch for a version with greater performance if needed. Apache was an obvious option for its platform independency. This is the reason for the use of Java programs, too. These components allow installing the system on almost any platform.

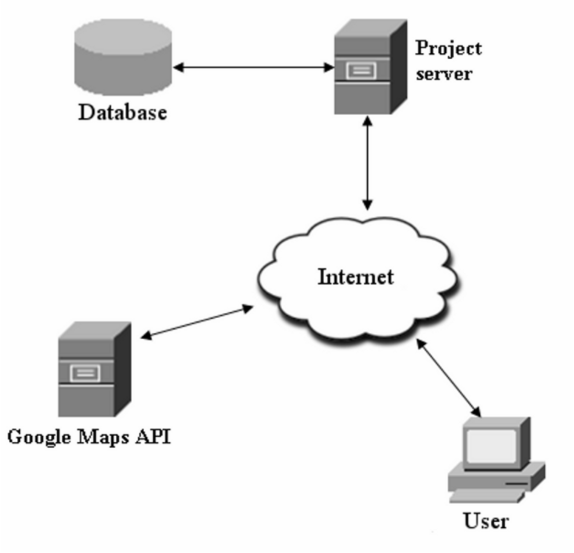


Figure 4. Connection of components.

The integration of Google Maps API enables using a solid interface known by many for in-map data visualization. Its further advantage is that storing project-independent map data does not demand any resources from the university. Data is stored by Google and the users get them from their databases. GIS information supplementing measured data (i.e. streams and coordinates) were digitized using Arc view 3.2. These files are stored on server of the project. In Figure 4 the connections of these elements are shown.

3.1. HOW TO USE THIS SYSTEM?

Any information concerning the system and the project is easily accessible via drop-down menus from the index page (Figure 5). Elements of the drop-down menu are static HTML 4.01 pages.

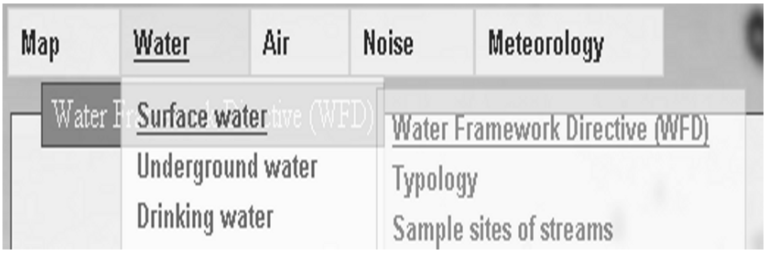
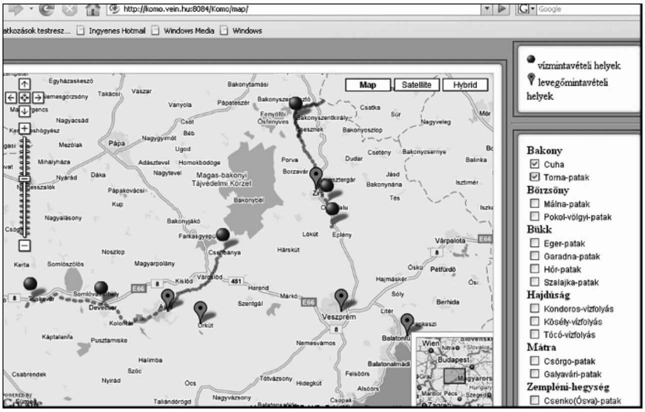


Figure 5. Structure of index page.

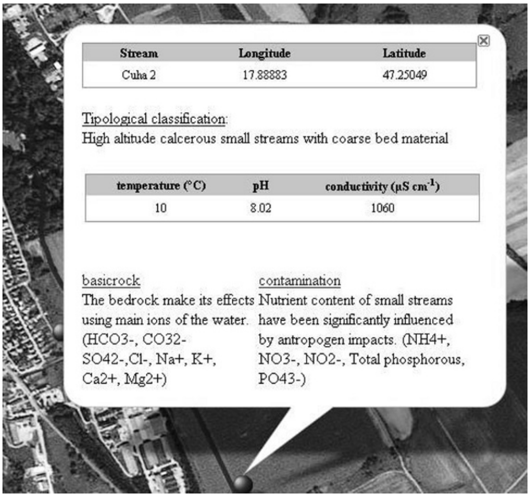


Bakony
☑ Cuha
☑ Toma-patak
Börzsöny
☐ Málna-patak
☐ Pokol-völgyi-patak
Bükk
☐ Eger-patak
☐ Garadna-patak
☐ Hór-patak
☐ Szalajka-patak
Hajdúság
☐ Kondoros-vízfolyás
☐ Kösély-vízfolyás
☐ Tócó-vízfolyás
Mátra
☐ Csórgo-patak
☐ Galyavári-patak
Zempléni-hegység
☐ Csenko(Ósva)-patak

Figure 6. Data visualization on Google Map.

Using the dynamic pages users can reach the “Map” menu serving as the first step of data visualization.

Appearance of demanded streams is possible if you put a tick of the name of stream (Figure 6).



Stream	Longitude	Latitude
Cuha 2	17.88883	47.25049

Tipological classification:
High altitude calcerous small streams with coarse bed material

temperature (°C)	pH	conductivity (μS cm^{-1})
10	8.02	1060

basicrock
The bedrock make its effects using main ions of the water. (HCO3-, CO32- SO42-,Cl-, Na+, K+, Ca2+, Mg2+)

contamination
Nutrient content of small streams have been significantly influenced by antropogen impacts. (NH4+, NO3-, NO2-, Total phosphorous, PO43-)

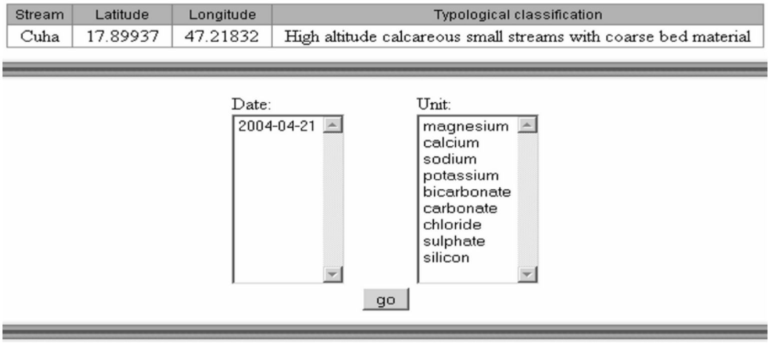
Figure 7. Generic information about upper reach of Cuha stream.

Popup windows (Figure 7) show only basic information from data collected on the site. User can see typological classification and parameters measured on the field. Other possibility for users is receiving information about effect of bedrock to water and pollutants level of watercourses. These data were stored in a database after manual screening. The aim of this step is to select and discard faulty data. Faulty data could significantly slow down, complicate, or in some cases make interpretation impossible of the outcome given by automatic processing. In the popup window (Figure 7) the user may choose to go to a new page where measured essential chemical parameters (eight main ions and N and P forms) are displayed (Figure 8).

On the homepage bar charts show measured values at different sampling sites of the streams. This bar chart shows the hydro-geochemical differentiation of the typology (Figure 9).

These provide generic information about condition of watercourse comprehensible for everyone. The system relieves users to query data since those bar charts and figures may be inquired from the database, which provide the needed information. *The internet's address (Environmental Information System): http://okoret.uni-pannon.hu*.

Examined values were presented on map due to easier evaluation and introduction of water quality.

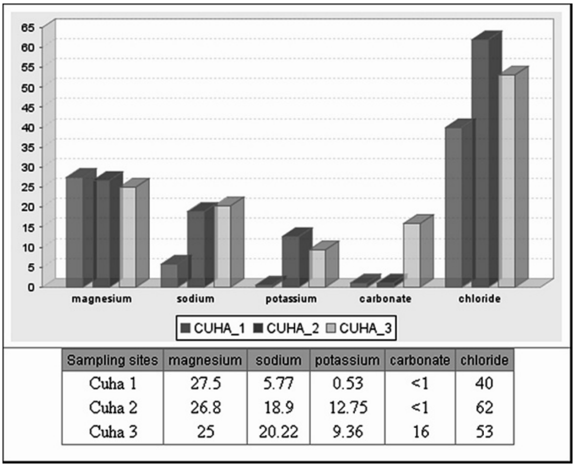


Stream	Latitude	Longitude	Typological classification
Cuha	17.89937	47.21832	High altitude calcareous small streams with coarse bed material

Date: 2004-04-21

Unit:

Figure 8. Searching according to measurement periods and chemical parameters.



Sampling sites	magnesium	sodium	potassium	carbonate	chloride
Cuha 1	27.5	5.77	0.53	<1	40
Cuha 2	26.8	18.9	12.75	<1	62
Cuha 3	25	20.22	9.36	16	53

Figure 9. Representation of some chemical parameters of Cuha stream using a bar chart.

3.2. APPEARANCE OF RESULTS

With cluster analysis based on the main ions calcareous and siliceous waters were distinguished. Dendogram on the main ions have supported the hydrogeochemical differentiation of the typology. High sulphate and chloride concentrations were measured at the lower reach of the Kösély stream. This proves that it does not belong to either of the two categories (Figure 10).

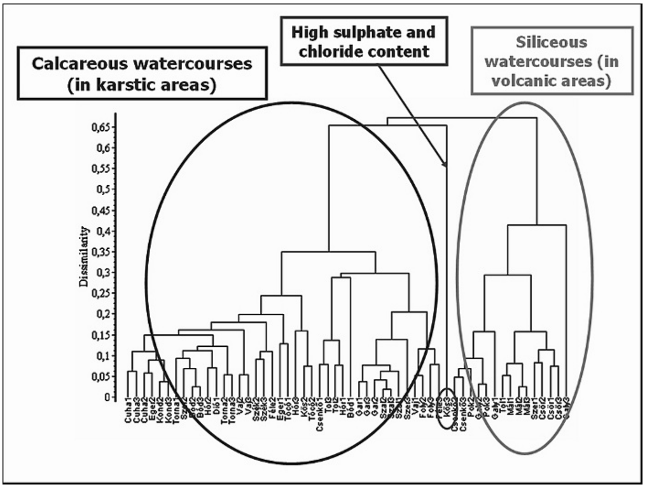


Figure 10. Dendogram (Bray-Curtis) of streams based on the main ionic (Ca^{2+}, K^+, Mg^{2+}, Na^+, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-) composition.

In the case of N and P forms only polluted sites were significantly different (Figure 11). Figure clearly shows that the middle reach of the Kösély and Tócó streams were different from the other streams as the measured N and P forms level were extremely high.

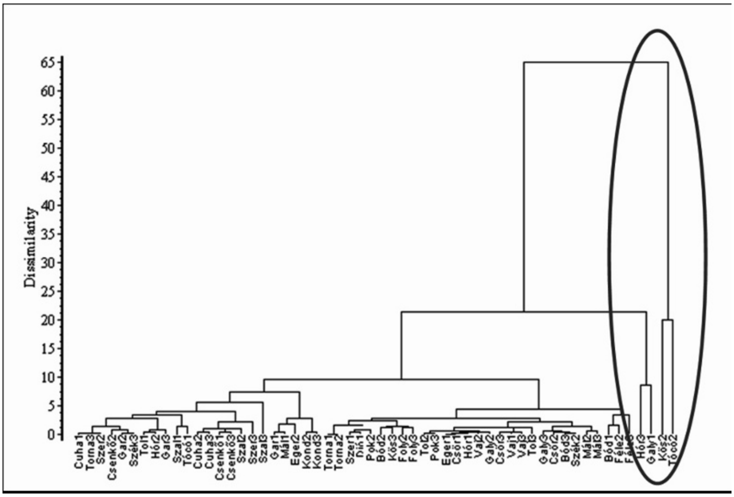


Figure 11. Dendogram according to nitrogen and phosphorus forms (Euclides).

3.3. VISUALIZATION

Examined values were presented on map (Arc View 3.2) due to easier evaluation and introduction of water quality. The polygon of the river was divided into to five parts resembling the different quality classes (from to down A-B-C-D-E) surface water was divided into small sections short by sample sites as well (Figure 12).

On the map it is clearly visible that according to measured concentration components in group A are categorised as excellent. Components (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}) in group B are categorised as strongly contaminated water. Components in group C group were not tested therefore the line stayed coloured i.e. white. In group D the following micro-pollutants (Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Pb^{2+}) were measured. According to measured values the Cadmium concentration was high so D was categorised as extremely contaminated water quality. Components (pH, conductivity, temperature, Na^+–, K^+–, Ca^{2+}–, Mg^{2+}–, Mn^{2+}–, $Fe^{2+/3+}$–, SO_4^{2}–) in group E are categorised as tolerable in accordance to the measured concentrations.

Figure 12. Fractional water qualification of Séd in Veszprém stream (homepage).

4. Conclusions

Cluster analysis on the main ions supported the hydrogeochemical differentiation of the typology: streams with calcareous and siliceous bedrock appeared in different group. Typological differentiation based on nutrition content was not possible because of the human impacts on these waters. According to the water quality measurement results can be stated that the quality of watercourses is mostly influenced by artificial or human impact pollution forms like sewage or cultivated lands and gardens. The main road is the other pollution source as organic compounds or heavy metals can be washed into the streams. The source and location have to be roughly determined. Not only is the prevention of surface water from pollutants important but it is very crucial to inform people (both experts and residents) about state of streams using Environmental Information System. To introduce the results in an informative way by bar charts and cluster analysis. Displaying the results on coloured scale helps to understand water condition for users. The developed homepage contains such techniques of visualization that makes it easily understandable for everybody. To provide an entire state assessment on the environment the measurements and results are needed to be permanently available. Tendencies of figures, bar charts, diagrams only provide useful information if they are based on sufficient data. Therefore the structure of the system allows further expansion and is able to measure other environmental elements such as meteorology data, air pollution and noise map.

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EDUCATIONAL APPROACH OF SAFETY AND RISK ASSESSMENT COURSES AT MASTER PROGRAM

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Abstract. This paper presents the experience in curricula development at high educational institutions level, by a group of 18 European universities, all having environmental related study programs. In the frame of the European Commission Socrates program, Erasmus action, Management and Security Assessment for Sustainable Environment – MASS project was approved in 2005 as a Curricula Development activity, and progressed during 2006–2007. The aim, objectives and main target groups of the MASS project are presented. MASS project creates the basis of framework for MSc programs, with possible extension to open and distance learning. The module type project, aimed developing three new courses, covering a large subject of interest nowadays, related to environmental impact assessment, environmental safety and risk assessment, sustainability of production and consumption. The main outputs of the project are the improved curricula and syllabus at master program. The three new courses were implemented at master level by all partners' universities, as new courses or updating/ completing existing courses.

Keywords: educational European projects, safety and risk assessment

1. Introduction

All across Europe, universities are engaged in modernisation processes. Coming to meet all the high educational institutions (HEI) efforts, the Bologna system

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proposed a framework able to create the European Education area in order to match the performance of students from different universities. One of the aims of Bologna process is to ensure the recognition of qualifications and periods of study.

In order to support these efforts, European Commission developed the European Socrates Program, where Erasmus action is part of the network, and the Curricula Development (CD) projects are granting educational groups to develop new or to update existing curricula, either for undergraduate-initial level (CDI), or for advanced level (CDA), either for an entire study program (PROG) or for part of the study program, as modules (MOD). Moreover, after CD projects, Socrates-Erasmus Program also finance dissemination projects (DISS), aiming to valorise the projects and their results (Draghici, 2006).

In this framework, universities from Romania and other European countries were involved in projects developed in partnership in order to achieving the Bologna system goals. In the context of sustainable development, environmental sciences are one of the important fields of study, in which many European universities are involved.

2. Curricula Development Projects Experience

Following the institutional policy and strategy, starting with 2000, Transilvania University of Brasov, Romania, was involved in upgrading and developing the existing curricula in the field of environmental sciences. In this context, the following projects were developed in partnership, between different European HEI, during 1-2-3 years each, with Transilvania University of Brasov, Romania, as coordinator:

1. Management of the Chemical Investigations in Environmental Protection, 2000–2003, CDI/MOD project
2. Management of the Chemical Investigations in Environmental Protection, 2003–2004, CD/DISS project
3. Bioanalytical Methods Linking Environmental Protection and Public Health, 2002–2004, CDI/MOD project
4. Bioanalytical Methods Linking Environmental Protection and Public Health, 2004–2005, CD/DISS project
5. eLab Information and Communication Technologies in Applied Chemistry, 2002–2005, CDA/PROG project
6. MASS – Management and Security Assessment for Sustainable Environment, 2005–2007, CDA/MOD project

Thirty-four high education institutions from 15 European countries participated and contributed to these six projects (Girotti et al., 2005; Draghici et al., 2004).

The first project, *Management of the Chemical Investigations in Environmental Protection*, developed courses on environmental pollution, environmental monitoring and waste management, mainly for undergraduate level. This project was followed by a DISS one on the same topic, when an international conference, Trends in Environmental Education (EnvEdu), was initiated. The first conference was in 2004, followed by the following ones in 2005 and 2006.

The *Bioanalytical Methods Linking Environmental Protection and Public Health* CDI/MOD and CD/DISS projects were focused on topics related to the effects of the pollutants on human health and the available bioanalysis able to relieve these effects. In the framework of this project two courses were also developed, mainly for undergraduate level and the second edition of EnvEdu conference was organised.

The *eLab Information and Communication Technologies in Applied Chemistry* CDA/PROG project developed and implemented at advanced level a new master study program, in partnership with other four European universities.

All these projects allowed developing and enforcing the study programs from the partners' universities, both at undergraduate and master level. The projects were also supported by students and teaching staff mobility, when educational and research experiences were exchanged among the involved institutions.

3. MASS – Management and Security Assessment for Sustainable Environment Project

Following the trend of the previous projects, and answering to the continuous need for curricula development at the Transilvania University of Brasov in environmental sciences and engineering, MASS – Management and Security Assessment for Sustainable Environment project was proposed in 2005, as a MOD type project at master level, approved and progressed during 2006–2007.

The aim of the MASS project was to develop a European module at master program in environmental sciences, by developing new courses and new joint educational methods, in order to ensure an appropriate educational strategy for dynamic knowledge acquisition, and to create the basis of framework for MSc programs, with possible extension to open and distance learning. The module, consisting in the three proposed courses, covered a large subject of interest nowadays, related to the environmental impact assessment, safety and risk assessment, and sustainability of production and consumption.

The main objectives were as follows:

- O1 to ensure the functional managerial frame of the project
- O2 to develop teaching materials for three courses
    - Environmental Impact Assessment (EIA)
    - Environmental Safety and Risk Assessment (ESRA)
    - Sustainable Production and Consumption (SPC)
- O3 to implement a joint educational method based on e-learning paradigm
- O4 to improve and update the existing infrastructure in the partner institutions according to the new educational method
- O5 to evaluate the project activities and products of the project
- O6 to disseminate the project activities and outcomes among the partners and other key actors according to the target groups
- O7 to create the basis of a future thematic network on environmental sciences education

The main target groups consists in postgraduate students, at MSc programs (possible open and distance learning programs), but the developed outputs could be also used at undergraduate level, Ph.D. programs and/or lifelong learners as well. The main activities were focused on courses development and implementation, based on an e-learning method.

MASS project partnership was formed by 18 universities, 14 initial partner institutions: from Romania Transilvania University of Brasov, Ovidius University of Constanta Babes-Bolyai University of Cluj-Napoca, University of Iasi, “Gh. Asachi” Technical University of Iasi and Politehnica University of Timisoara, from Bulgaria Technical University of Sofia, from France University of Perpignan, Ecole Centrale de Lyon, from Italy University of Milano, University of Trieste, from The Netherlands Delft University of Technology, University of Groningen and from Poland Technical University of Gdansk. After the project was granted other four universities entered as new partner institutions, without financial support from the EC Soctares program: from Italy University of Bologna and University of Torino and from Romania North University of Baia Mare and Politehnica University of Bucharest.

The main outputs of the project are the improved syllabus at master program with three new courses (in printed and electronic format), with a large contribution of the teaching staff from all 18 partners’ universities.

As a result of the involved HEI collaboration, the three courses were developed with a large contribution of the partners’, as given in Table 1.

TABLE 1. HEI partners' contribution to the courses content.

Partner institution	EIA	ESRA	SPC	Total contributions
Transilvania University Brasov, RO	1	1	1	3
Technical University of Sofia, Bulgaria, BG	1	1		2
University of Perpignan, FR	1	1	1	3
Ecole Centrale de Lyon, FR		1		1
University of Bologna, IT	1	1		2
University of Milano, IT		1		1
University of Torino, IT		1		1
University of Trieste, IT		1		1
Delft University of Technology, NL		1	1	2
University of Groningen, NL	1	1	1	3
Gdansk University of Technology, PL	1	1		2
North University of Baia Mare, RO	1	1	1	3
Ovidius University of Constanta, RO	1	1	1	3
Babes-Bolyai University of Cluj Napoca, RO	1	1	1	3
Al. I. Cuza University of Iasi, RO	1	1		2
Gh. Asachi Technical University Iasi, RO	1	1	1	3
Politehnica University of Timisoara, RO	1	1	1	3
Politehnica University of Bucharest, RO		1	1	2
Total universities contributing	12	18	10	

Of interest for this paper is the second course Environmental Safety and Risk Assessment that was developed under the responsibility and edited by specialists from Babes-Bolyai University of Cluj Napoca and Transilvania University of Brasov, both from Romania. The course covered the most important topics associated to the subject and was structured in tree main chapters: (i) theoretical principles of environment risk assessment, (ii) environmental risk assessment applications and exercises and (iii) environment risk assessment case studies.

In the first part of the course, the topics presented were related to the policies and legislative issues for environment risk assessment, hazard characterisation and risk identification, environment risk assessment process, methods and techniques for environment risk assessment, consequences analysis and risk management, control and communication.

The thematic was approached related to the domains like sustainable development, chemistry, biology, toxicology, engineering, geology, etc., from a multidisciplinary point of view, with expertise and experience in human health and ecological assessments for terrestrial, aquatic, atmospheric and building environments.

The second part, environmental risk assessment applications and exercises, was focused on environmental monitoring, examples on bioindicators, biomonitoring, microbiosensors being presented.

The third part, on environment risk assessment case studies was focused on different subjects like pesticide residues distribution in agricultural foods, consumers' risk in the province of Bologna, drinking water in Romania, major industrial accidents with dangerous substances, or accidents in transporting dangerous substances.

Forty authors were involved and contributed in developing the topics of this course, as presented in Table 2.

TABLE 2. Authors contribution.

Partner university	Number of contributors	Partner university	Number of contributors
Transilvania University Brasov, RO	2	Babes-Bolyai University of Cluj Napoca, RO	3
Ecole Centrale de Lyon, FR	3	Al. I. Cuza University of Iasi, RO	5
University of Perpignan, FR	2	Gh. Asachi Technical University Iasi, RO	4
University of Milano, IT	2	Politehnica University of Timisoara, RO	3
University of Trieste, IT	2	University of Bologna, IT	5
Gdansk University of Technology, PL	3	University of Torino, IT	3
Ovidius University of Constanta, RO	2	Politehnica University of Bucharest, RO	1

Courses were implemented at master program level at all partners' universities, as new courses or updating/completing an existing course. Moreover, the courses were included in existing master programs or in new introduced ones. For example, new master programs, including these courses, will be started with the academic year 2008–2009 in three of the partners' universities and starting with the academic year of 2009–2010 in two more universities. Course implementation in the 18 partners universities is represented in Table 3.

TABLE 3. Course implementation.

Partner institution	Course implementation*		
	C1–EIA	C2-ESRA	C3-SPC
1. Transilvania University Brasov, RO	EM, NC, O NM, NC, C (2009)	EM, NC, O NM, NC, C (2009)	EM, NC, O NM, NC, C (2009)
2. Technical University of Sofia, Bulgaria, BG	EC, NC, O	EC, NC, O	EC, NC, O
3. Ecole Centrale de Lyon, FR	EM, EC, C	–	–
4. University of Perpignan, FR	EM, EC, C	EM, EC, C	EM, EC, O
5. University of Milano, IT	EM, EC, C	NM, EC, C	EM, EC, C
6. University of Trieste, IT	EM, EC, C	EM, EC, C	EM, EC, O
7. Delft University of Technology, NL	–	–	EM, EC, C
8. University of Groningen, NL	–	EM, NC, O	EM, EC, C
9. Gdansk University of Technology, PL	– NM, NC, O (2009)	– NM, NC, O (2009)	EM, EC, O NM, NC, O (2009)
10. Ovidius University of Constanta, RO	EM, EC, C	EM, NC, C	EM, NC, O
11. Babes-Bolyai University of Cluj Napoca, RO	EM, EC, C	EM, EC, C	EM, NC, C
12. Al. I. Cuza University of Iasi, RO	EM, NC, C NM, NC, C (2008)	EM, EC, C	–
13. Gh. Asachi Technical University Iasi, RO	EM, EC, C	EM, EC, C	EM, EC, C NM, NC, C (2008)
14. Politehnica University of Timisoara, RO	EM, NC, O	EM, NC, O	EM, NC, O
15. University of Bologna, IT	NM, EC, O	NM, EC, O	NM, EC, O
16. University of Torino, IT	EM, EC, C	NM, EC, C	EM, EC, C
17. North University of Baia Mare, RO	EM, EC, C	EM, EC, C	EM, NC, O
18. Politehnica University of Bucharest, RO	EM, EC, C	NM, NC, C (2008)	–

*Existing master program (EM); new master program (NM)
Updating/completing an existing course (EC); new course developing (NC)
Compulsory course (C); optional course (O)

The dissemination activity was carried out during the whole project life time, mainly with the occasion of conferences, training sessions and other scientific or professional events, by making project presentations, organizing dedicated workshops. All these dissemination activities had strong impact on the specific target groups, showing their interest in the new developed courses, appreciating that the teaching materials are useful for a large target audience.

4. Conclusions

The partnership was selected based on former collaborations, on the experience exchange among universities with different backgrounds and expertise in educational or research projects. This gave the European dimension to the MASS project, and the diversity of the partners experience and expertise was the premises of the project success.

The achievements of all seven Curricula Development projects were not only their main outputs, strictly official, like study programs, syllabus, teaching materials (courses) are. On our opinion, the major achievement is the extension to a real and fruitful collaboration between the partners, as a premise for further developments in educational and research activities.

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CASE STUDY OF THE RISK ASSESSMENT OF NITRATES ON HUMAN HEALTH IN THE WEST SIDE OF ROMANIA

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Abstract. Human exposure at chemical risks owes both to environmental factors (air, water) and food (vegetables, meat, milk, honey, etc.). These factors act simultaneously and cumulatively, the effects of certain wastes and contaminants are very complex and difficult to assess. In this paper, the risk assessment of nitrates for the inhabitants from West side of Romania is reported. Nitrates are processed from animal food (meat and meat products, milk and milk products), vegetables (spinach, salad, potatoes) and drinking water coming from local water sources, which are uncontrolled and very much polluted with nitrogen compounds. The estimated daily dose (EDD) was calculated for two scenarios, both for adults and children. The risk of nitrates ingestion at adults expressed as HR (Hazard Ratio) was sub-unitary and therefore, negligible. The risk of nitrates ingestion at children as HR was over-unitary but very close to 1, and can be removed by using water from controlled water sources and a special diet, which consists of vegetables from "without risk" series from this point of view.

Keywords: exposure, risk assessment, nitrates, hazard ratio

1. Introduction

The impact of nitrogen based compounds on human health is due to both the environmental factors (air, water) and food. Human exposure at nitrogen based compounds processed from food depends on several factors, i.e., age that is

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linked to body weight, culinary habits, season (winter salad is richer in nitrates), climate conditions (crop enhancement by fertilizers applying), type of crop, cultivation method (green house/in field). Tacking into account the water sources, groundwater plays a major role in the chemical risk of nitrogen-based compounds on human health. Groundwater pollution with nitrogen-based compounds is due either to the infiltrations of animal and human dejections or to the wrong usage of nitrogen based fertilizers in the past (Burtică et al., 2005). Nitrates and nitrites ingested through water and food are based on the continuous interchange relation, function of the presence or the absence of certain compounds. Water pollution with nitrates enjoys a growing interest because the presence of these compounds has lately been acknowledged and has a non-uniform character (Micu et al., 2006). Their toxicity on human health is due to the biochemical conversions of nitrates into nitrites and vice versa, and to the combination of sanguine haemoglobin with nitrites, forming methaemoglobin, through an irreversible process. The risk is very high for children, who are very exposed because of the small volume of their blood and of the alkaline pH for small babies, which is a suitable medium for the reduction of nitrates to nitrites.

Romania has a great incidence of methaemoglobinemia, with a significant death rate. For the period between 1984 and 1995, there were recorded 2,346 cases of methemoglobinemia for babies and 80 deceases. Moreover, there are signs that this number is underestimated because of the diagnostic difficulty. In 1988, 36% of the Romanian fountains showed nitrates concentrations over 45 mg/L. In Iasi county, for example, from only two sporadic cases of methaemoglobin found 20 years ago, recently cases hundreds per year have been overtaken. Also, the nitrites are the cause of gastric cancer via nitrozamine formed under certain conditions.

Vegetable products can contain high quantities of nitrates, as an effect of crop fertilization to reach the good yield. The highest quantities of nitrates are found in salad, spinach and potatoes, and are function of sort, season, fertilization type, and climate conditions. In Romania, the maximum allowance concentration of nitrates in spinach and salad regulated by Ordinance no. 438/2002 is 3,000 mg/kg (ORDIN MAPAM 438).

Food, in general and meat and meat products, in particular contain various quantities of nitrates. Sodium/potassium nitrates are added to product both for technological and antibactericide reasons and as preservatives. They have the capacity to delay the oxidative process and block the Botulinum Toxin, as well as to confer on meat a pink and nice commercial aspect. In Romania, the maximum allowance concentration of nitrates regulated by Ordinance no. 438/2002 is a function of food type, i.e., 250 mg/kg for meat products, 200 mg/kg for canned fish and fat and 50 mg/kg for cheese.

The aim of this study was to assess the risk of nitrates on human health for West side of Romania, expressed as hazard ratio (HR). The estimated daily dose (EDD) was calculated based on two scenarios, one for adults and the other for children, and the scenarios take into account the ingestion of nitrates from water, vegetables and meat products.

2. Experimental

For risk assessment expressed as Hazard Ratio (HR), the first step is to determine Estimated Daily Dose (EDD) as the sum of the components from water, vegetables and sausages. In addition, the major component of risk produced by nitrates was determined.

EDD was determined by summing the effects of ingestion of water, vegetables and sausages, which contain nitrates (Coquet, 2007).

Two scenarios were established, one for adults and the other for children, with specific criteria. For adults, it was assumed a body weight of 70 kg, who uses 2 L water/day (nitrate concentration = 90 mg NO_3^-/kg), 250 g potatoes/day (nitrate concentration = 250 mg NO_3^-/kg), 50 g salad/day (nitrate concentration = 800 mg NO_3^-/kg) and 50 g processed meat products/day (nitrate concentration = 35 mg NO_3^-/kg). The nitrate concentrations from water, potatoes and salad were determined experimentally for the sites near Timisoara city, from West side of Romania, and the nitrate concentrations from processed meat products are based on the field literature (Roman, 2005). It was assumed the exposure rate of 50% from the total time, supposing a recent pollution, and that the person was born in a different unpolluted side of the country. For children, it was considered a 12 years old child and with a body weight of 35 kg, who uses 1 L water/day (nitrate concentration = 90 mg NO_3^-/kg), 150 g potatoes/day (nitrate concentration = 250 mg NO_3^-/kg), 50 g salad/day (nitrate concentration = 800 mg NO_3^-/kg) and 50 g processed meat products/day (nitrate concentration = 35 mg NO_3^-/kg) (Roman, 2005). It was assumed the exposure rate of 80% from the total time as children's life time spent in a polluted environment.

EDD was calculated based on the formula (Coquet, 2007):

$$EDD_1 = \sum \frac{\text{Concentration} \times \text{Quantity administered} \times \text{exposure rate}}{\text{Body weight}} \qquad (1)$$

The risk assessment expressed as Hazard Ratio (HR) was determined with (ORDIN 438/2002; JECFA, 1995; JECFA, 2002):

$$HR = \frac{\text{Estimated Daily Dose}}{\text{Accep table Daily Intake}} \quad (2)$$

To estimate the human exposure to nitrates due to water ingestion, during the period of 2005–2006 it was analysed 166 groundwater samples and the results were compared with maximum concentration allowance (Legea no. 458, 2002). The groundwater proceeded from local water sources from rural plain of Timis county. Also, it was collected data about the usage degree of water proceeded from centralized water sources and data about the specific activities with pollutant character that occur in that area. Based on these data, it was concluded the usage degree of phreatic water and implicit the habitant exposure at nitrates.

The analysis methods used for water samples were in according with Romanian standards (STAS 3048-2, 1996).

To estimate the human exposure to nitrates due to the ingestion from vegetables, it was analysed a number of 21 vegetable samples, especial those mentioned in the literature as containing high content of nitrates (salad, spinach, potatoes) (Radulescu et al., 2005). The determination method of nitrates was Griess method, consisting of nitrate reduction to nitrite on cadmium column (STAS 11581-83).

3. Results and Discussions

Table 1 shows the assessment of underground water pollution with nitrates and the usage degree of this water by the inhabitants.

Figure 1 shows the results of nitrates determination from the vegetables coming from Timisoara's markets. For all determinations, no maximum concentration allowance was reached.

Nitrates (Table 2) themselves in their initial form do not have a toxic nature regarding human health, but they may become so by their endogen conversion into nitrites, right in digestive tract. At its 44th meeting, JECFA concludes that the range of nitrate conversion is 5–7% for normal individuals and 20% for individuals with a high rate conversion. The ADI for nitrate is 0–3.7 mgNO_3^-/kg bw/day, respectively 0–5 mg $NaNO_3$/kg bw/day.

TABLE 1. The status of water supply from uncontrolled and polluted water sources from West side of Romania.

Settlement	Population using uncontrolled water* (%)	Water sample no	NO_3^- mg/L	Settlement	Population using uncontrolled water* (%)	Water sample No	NO_3^- mg/L
Banloc	75	16	0–**100**	Lovrin	77	7	0
Becicherec	0	8	0–**115**	Masloc	NP	10	0–**110**
Belint	94	1	–0	Mosnita noua	100	1	5
Biled	12	6	0–**115**	Ortisoara	NP.	1	**50**
Birda	100	2	0	Padureni	100	1	0
Bogda	NP	1	**75**	Peciu nou	NP	3	0
Ciacova	NP	3	0	Periam	73	15	0–**400**
Comlosu mare	0	2	0	Pischia	88	10	0–**110**
Fibis	NP	6	**70–90**	Recas	NP.	4	0–50
Foeni	0	1	0	Satchinez	97	1	10
Ghizela	NP	4	0	Sacalaz	38	1	0
Giera	NP	1	50	Sanandrei	0	4	20–**90**
Giroc	NP	10	**5–90**	Sag	77	8	0–**100**
Giulvaz	69	2	2–50	Topolovat	90	2	0–5
Lenauheim	38	1	0	Varias	75	18	0–**115**
Liebling	43	2	0–25	Voiteg	53	2	0
Sandra	100	2	0–**100**				

* For 2005 year.

TABLE 2. Nitrates contents and maximum concentration allowance (MCA) of some vegetables, (ORDIN 438/2002) (*NS-nonstandardized).

	Spinach	Salad	Potatoes	Cucumber	Carrot	Tomato	Water melon
Mg $NaNO_3$/kg	500	800	250	0	0	0	0
No. analyzed samples	6	6	6	6	6	6	6
CMA, mg $NaNO_3$/kg	3,000	2,000	NS*	NS*	NS*	NS*	NS*

The EDD (estimated daily dose) for nitrates was calculated by summing up the contributions of water and vegetables based on the above-mentioned formula (Equation 1).

Although both the nitrates concentration found and the CMA (50 mg/L) in drinking water are not so high by comparison with the other components taken into account, drinking water showed the highest contribution to the EDD (Figure 1).

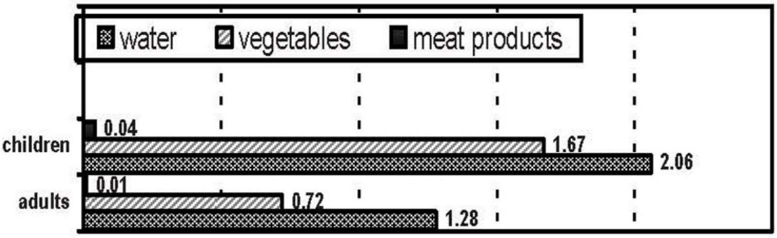

Figure 1. Graphical representation of the different components, which subscribe to the EDD.

The hazard ratio (HR) for both scenarios was calculated, $HR_{adult} = 2.01/3.7 = 0.54$ and $HR_{children} = 3.81/3.7 = 1.03$.

Table 3 shows the EDD and HR for both scenarios, and there can be concluded that the risk of nitrates on human health for adults is negligible (HR < 1), while for children the HR > 1, but very near to 1 (1.03), which means that the risk of nitrates is present. Because the body weight plays the most important role for HR, the younger the children, the higher the risk of nitrates on their health.

Nevertheless, the risk of nitrates exposure is present not only for children; on the contrary, there is one for the whole community, as about 65% of the rural inhabitants from West side of Romania (Timis county) use daily drinking water from sources that are uncontrolled and polluted with nitrates. It has to be underlined that the risk of nitrates is very variable because of different culinary habits, the permanent modification of the groundwater, different ages of the inhabitants, and different conversion rates from nitrates to nitrites.

TABLE 3. EDD and HR evaluation of nitrates for adults and children.

	Adults	Children
EDD	2.01	3.87
HR	0.54	1.03

4. Conclusions

Each food that contains nitrates, e.g., water, vegetables and meat products contributed in a certain degree to the risk on human health in West side of Romania.

Even if the CMA for water is smaller than CMA's for meat and vegetables, drinking water showed the highest contribution to the risk of nitrates to human health because the exposure is higher.

Taking into account that about 65% from the rural inhabitants in Timis county, West side of Romania, have been using drinking water from uncontrolled and polluted water sources, it is imperative to establish a centralized water supply system in this part of the country. As a transitory measure, it is required that each inhabitant should control drinking water from their household and avoid its usage if it is not suitable.

Also, vegetables showed an important contribution to the risk because of their high content of nitrates, e.g., spinach and salad and by permanent exposure, e.g., potatoes, that is basic food for Romanian rural inhabitants.

Taken separately, each component of water, vegetables and meat products have no negative effects on human health, but the association of these components may sometimes lead to a grown risk on human health, especially for children.

The future work will take into account the risk of nitrites based on the analysis of nitrites in food and the different conversion rates of nitrates into nitrites.

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LEVELS OF POLYCHLORINATED BIPHENYLS AND POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS NEARBY METALLURGICAL PLANT KREMIKOVTSY

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Abstract. Persistent organic pollutants (POPs) such as the polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants. They are highly persistent and tend to accumulate in many environmental compartments including soils. But the concentration and distribution of POPs in the environment have not been well studied in Bulgaria in spite of their negative effect on the environment and human health. In this study, soil samples from a metallurgical plant Kremikovtsy were analyzed for indicator PCBs and PAHs. The sums of concentrations of indicator PCBs were in the range 5.6–18.2 μg kg^{-1}. High chlorinated indicator PCBs – 138, 153 and 180 were the most abundant in the soil samples. The ranges of PAHs concentrations in the soil samples were 352–437 μg kg^{-1}. PCBs and PAHs concentrations found in this study are below the maximum admissible concentrations in soils according to the Bulgarian Legislation.

Keywords: Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), soil, metallurgical plant

1. Introduction

Persistent organic pollutants (POPs) such as the polychlorinated biphenyls (PCBs) and polycyclic aromatic compounds (PAHs) are a set of chemicals that are toxic, persistent in the environment for long period of time and biomagnify

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as they move up through the food chain. POPs are linked to adverse effect on human health and animals, such as cancer, damage to the nervous system, reproductive disorders and disruption of the immune system. Because they circulate globally via the atmosphere, oceans and other pathways, POPs released in one part of the world and can travel to regions far from their source of origin (UNEP, 2005).

Dry and wet atmospheric deposition constitutes the main input of semivolatile organic compounds to soil (Tremolada et al., 1996). POPs are transported in the atmosphere at over short and long distances in both gaseous and particulate forms. Because of their persistence and hydrophobicity, these omnipresent compounds accumulate in soils where they are likely to be retained for many years. Consequently, soils are an important reservoir for these toxic substances (Ockenden et al., 2003).

PCBs and PAHs concentrations measured in soils are significantly correlated with those in the atmosphere and therefore, soil POP levels are a good indicator of the surrounding air pollution and the proximity sources (Wilcke et al., 1996).

In spite of negative effects on the environment and human health the concentration and distribution of POPs in the environment have not been well studied in Bulgaria (Rizov, 2005).

The aim of this work was to determine the levels of indicator PCBs (28, 52, 101, 138, 153 and 180) and PAHs (NAP, ACY, ACE, FLU, PHE, ANT, FTH, PYR, BaA, CHR, BbF, BkF, BaP, DahA, BghiP, IcdP) in soil samples taken from the territory nearby the metallurgical plant Kremikovtsy.

2. Materials and Methods

2.1. THE METALLURGICAL PLANT KREMIKOVTSI

The plant Kremikovtsy is located in the north-eastern Sofia valley, close to the city of Sofia. The plant covers the full metallurgical cycle – from output of iron ore to ready products – cast iron, steel and ferrous alloys. It also produces tin-plated sheet iron and metalloplasts.

The industrial activities began during the 1960s. According to the amounts of production, it is the most important metallurgical complex of Bulgaria. The plant was identified as important source of inorganic contaminants. But it is likely source of persistent organic pollutants (PCBs, PCDDs/Fs and PAHs), too.

2.2. MATERIALS

Solvents (dichloromethane and n-hexane) were of analytical grade quality (Merck, Darmstadt, Germany). Anhydrous sodium sulfate and silica gel

(70–230 mesh ASTM) were also from Merck. Cellulose extraction thimbles were from Whatman Ltd. (Maidstone, England). Cellulose thimbles were cleaned by Soxhlet extraction with dichloromethane before analysis. Standards of PCBs and PAHs were from Dr. Ehrenstorfer (Augsburg, Germany).

2.3. SAMPLE COLLECTION AND PREPARATION

Soil samples were collected using the "envelope" method (five individual subsamples – four along the boundaries and one in the center). They were taken from the topsoil – 10 cm) over a $50m^2$ area typical for the site. Subsamples were combined and carefully homogenized and then an average sample weight of approximately 1 kg was taken.

Eight average soil samples were prepared. All soil samples were collected at 3 km distance around the plant in all directions.

The soil samples were air dried ground and sieved through a <2 mm sieve before extraction.

2.4. EXTRACTION

Soil samples were weighed into Whatman Soxhlet cellulose thimbles, spiked with internal standards, covered with anhydrous sodium sulfate and extracted by Soxhlet technique for 18 h with dichloromethane: hexane (1:1). All extracts were concentrated by rotary vacuum evaporator to 1 mL. The concentrated organic extracts were cleaned with an acid-base-silica column. Organic compounds were eluted with 50 mL dichloromethane. Elution solvents were concentrated to 1 mL in dichloromethane after rotary vacuum and nitrogen stream evaporation.

2.5. INSTRUMENTAL ANALYSIS

The analysis was performed with Hewlett Packard Model 5890 Series II PLUS gas chromatograph equipped with Hewlett Packard 5972 Mass Selective Detector (GC/MS). HP-5 fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 µm film thickness) coated with 5% phenyl–95% methylpolysiloxane was used for the analysis.

The column oven temperature program started at 120°C (holding time 1 min), increased to 190°C at 20°C min^{-1}, increased to 230°C at 5°C min^{-1} and finally to 300°C at 25°C min^{-1} (holding time 10 min). Injector and detector temperatures were 280°C and 300°C, respectively. Helium was used as carrier gas at a constant flow rate of 0.8 mL min^{-1}. Injection was performed in splitless mode.

The mass spectrometer was operated in electron impact ionization (EI) – positive-mode using automatic gain control and selected ion monitoring (SIM). The scan time during data acquisition was set at 1.0 s with four microscans per second.

PCBs were quantified by comparison with an external standard mixture (MIX 20) composed of PCB 28, 31, 52, 77, 101, 105, 118, 126, 128, 138, 153, 156, 169, 170 and 180. The detection limits for the substances was 0.15 µg kg^{-1}. PCB concentrations were expressed by the six congeners of the European norms (28, 52, 101,138, 153 and 180).

For PAHs the solution of a standard mixture MIX 9 containing the 16 PAHs (NAP, ACY, ACE, FLU, PHE, ANT, FTH, PYR, BaA, CHR, BbF, BkF, BaP, DahA, BghiP, IcdP) was used. Under our analytical condition, detection limits ranged from 0.04 to 0.4 µg kg^{-1}, depending on the PAH analyzed.

Results of blanks extracted under the same conditions were below detection limits and sample results were displayed without blank correction.

3. Results and Discussion

This paper reports the results obtained from an initial study in the metallurgical plant Kremikovtsy near Sofia, for levels of soil contamination with indicator PCBs and PAHs.

TABLE 1. Concentrations of PCBs in soil samples (µg kg^{-1} d. w.).

Samples	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	Σ PCBs
Soil 1	1.4	1.5	1.6	2.6	2	1.7	10.8
Soil 2	1.7	1.4	1.5	1.9	2.3	1.6	10.4
Soil 3	1.3	1.2	2.4	5	3.6	4.7	18.2
Soil 4	0.2	1.9	2	2.9	2	1.8	10.8
Soil 5	1.3	1.2	2.1	2.3	2.1	1.8	10.8
Soil 6	2.1	1.8	2.6	3.3	2.7	2.1	14.6
Soil 7	0.2	0.5	0.2	1.4	1.1	2.2	5.6
Soil 8	1.4	1.5	1.6	2.6	2	1.7	10.8
Mean	0.8	1.1	1.2	2.5	2.0	2.6	18.2
SD	0.66	0.50	0.84	0.87	0.59	1.18	4.63

3.1. PCBS CONTENT AND DISTRIBUTION IN SOIL

PCBs concentrations in soil samples are summarized in Table 1. Analyzed indicator PCBs were detected in all samples. Concentrations of the six indicator congeners ranged from 5.6 to 18.2 µg kg^{-1}, with a mean value of 10.2 µg kg^{-1}, and were below the maximum admissible concentrations (MAC) of 200 μg kg^{-1} in soils according to the Bulgarian Legislation (Regulation Number 3 Concerning Limit Values of Hazardous Substances in Soil; State Gazette, Sofia, No. 39/2002). They are also below the precautionary target values (20 μg kg^{-1}), but exceed the referent background values (5 μg kg^{-1}) as set by the ordinance. Accordingly, it can assume that the Kremikovtsy soils were not severely contaminated by PCBs.

The levels of PCBs in soils near Kremikovtsy plant were much lower than those in soils adjacent to industrial areas in the Seine River basin in France, where the average value of Σ I-PCBs reached 73.9 μg kg^{-1} (Motelay-Massei et al., 2004). The range of PCBs concentrations found in this study was lower also than that reported for soils from industrial areas of Taiwan: 94.9 μg kg^{-1} (Thao et al., 1993), Austria: 6.4–95 μg kg^{-1} (Weiss et al., 1994) and Poland: 4.6–3,400 μg kg^{-1} (Falanysz et al., 2001). In Romania, Covaci et al. (2001) found average contents of 57.3 and 722 μg kg^{-1} for urban and industrial sites, respectively. Notarianni et al. (1998) reported an average value of 25 μg kg^{-1} for urban sites in northern Italy.

The individual distribution of each of indicator PCBs was presented on a Figure 1. The hexachlorinated PCB 138, PCB 153 and heptachlorinated PCB 180 were most abundant in soil samples. This may be due to their higher hydrophobicty and affinity for strongly adsorption with soil organic matter.

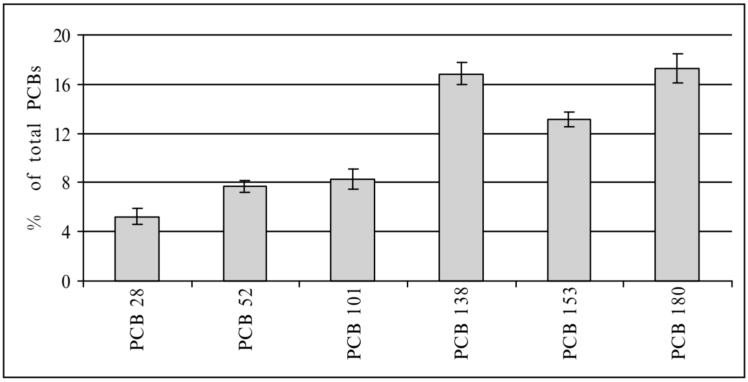

Figure 1. Average PCB congener profiles of soils 1–8 (error bars indicating standard deviations).

3.2. PAHS CONTENT AND DISTRIBUTION IN SOIL

PAHs were detected in all soil samples, presumably sourced from local manufacture activity of the metallurgical plant and deposition of contaminated ashes and wastes. Concentrations of PAHs in samples ranged between 352 and 437 µg kg^{-1} (Table 2). The mean concentration was 401 µg kg^{-1} for all samples together. These concentrations are below the MAC of 4,000 µg kg^{-1} in soils according to the Bulgarian Legislation, but they are in the range of the precautionary target values (400 µg kg^{-1}) as set by the ordinance.

TABLE 2. Concentrations of PAHs in soil samples (µg kg^{-1} d. w.).

Samples	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Mean	SD
NAP	42	29	40	51	45	44	52	50	44	0.45
ACE	18	12	17	7.5	10	15	17	13	14	0.59
ACY	7	4	5	6	8	5	6	8	6	0.54
FLU	4.6	4.6	8.3	20	8.7	8	10	11	9	0.28
PHE	55	35	51	38	59	48	52	40	47	0.66
ANT	11	6	5	5	4	7	8	10	7	0.48
FTH	7	5	4	3	8	5	7	7	6	0.53
PYR	24	18	18	15	23	20	19	18	19	0.52
BaA	16	38	33	35	27	31	33	38	31	0.43
CHR	7	13	11	16	6	8	10	11	10	0.42
BbjkF	21	20	20	13	29	24	29	26	23	0.23
BaP	36	34	41	24	48	37	39	35	37	0.40
BeY	21	16	14	14	15	19	22	25	18	0.25
IcdP	59	47	45	52	56	51	48	42	50	0.31
DghiP	24	25	32	35	22	34	34	29	29	0.37
BgniP	54	46	58	47	46	44	51	49	49	0.49
ΣPAHs	406.6	352	402.3	381.5	414.7	400	437	412	401	0.46

According to the classification established by Maliszewska-Kordybach (1996), as summarized in Table 3, all of the soil samples can be considered as weakly contaminated. The threshold values of this classification (200, 600 and 1,000 µg kg^{-1}) were derived from the results of determinations of PAHs concentrations in European soils, as well as from an estimation risk of human exposure (Paterson and McKay, 1989).

Determined PAHs concentrations were much lower in comparison with those of other countries. For example, in Estonia was measured PAHs concentration between 2,200 and 12,300 µg kg^{-1} (Trapido, 1999), in USA – 3,700 µg kg^{-1} (Mielke et al., 2001) and in France – 5,650 µg kg^{-1} (Motelay-Massei et al., 2004).

These comparisons indicating that the Northeastern industrial part of Sofia was not grossly polluted by PAHs.

The individual contribution of each PAH was presented on a Figure 2. The predominant compounds were naphtalele (11% on average), phenanthern (11.79%), indeno(cd)pyrene (12.47%) and benzo(gni)perylene (12.31%). On the whole, the PAHs with the highest molecular weights were predominant in soil, the lighter ones being easily degraded or exported.

TABLE 3. Classification of soil contamination by PAHs. (From Maliszewska-Kordybach, 1996.)

Class of soil contamination	Σ 16 PAHs (μg kg^{-1} d.w.)
not contaminated	<200
weakly contaminated	200–600
contaminated	600–1,000
heavily contaminated	>1,000

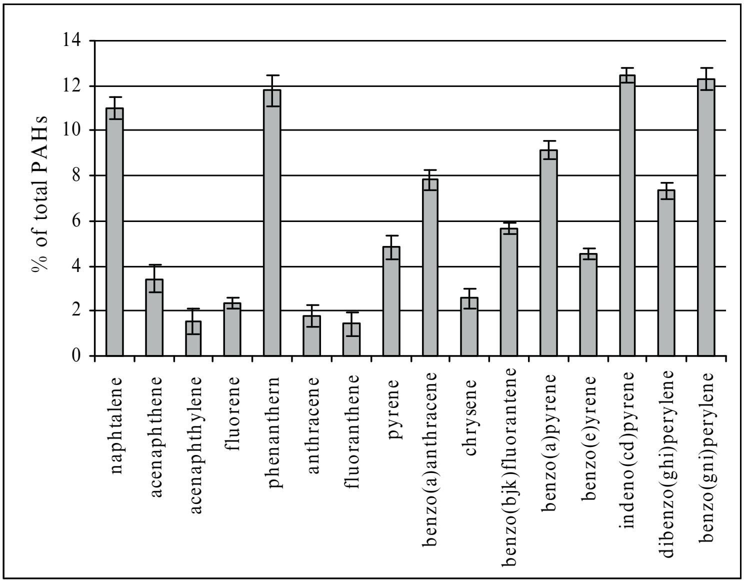

Figure 2. Average PAH profiles of soils 1–8 (error bars indicating standard deviations).

4. Conclusion

Kremikovtsy plant produces cast iron and steel. The plant is a probable source of POPs because in thermal metallurgical processes such as ferrous foundry and metal smelting operations, large flows of off-gases are generated. And organic compounds are always present in the feed. Nevertheless up to that moment POPs contents in soils at the plant territory and around it have not been monitored.

The present initial study has provided the first data on the levels of indicator PCBs and PAHs in soils nearby the metallurgical plant.

The results indicated that individual PCBs and PAHs present in all soil samples. The high chlorinated biphenyls (hexa- and hepta-CBs) were predominated in the samples. PAHs with higher molecular mass were dominated in soils, too. The probable reason is that low compounds are more volatile while the higher are more adsorbed to soil particles.

The levels of PCBs and PAHs found in this study are below the maximum admissible concentrations of the Bulgarian Legislation. But for PAHs determined levels are about precautionary target values. That is why regular monitoring would be advisable.

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SUBJECT INDEX