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Toxic Substances Management in Lakes and Reservoirs

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FOREWORD

S. Evteev

Natural and synthetically-produced chemicals represent a major paradox in our modern world. Millions of different chemical substances are used daily around the world, and have proven to be very beneficial to mankind in many ways. Examples of beneficial uses include destruction of disease-carrying organisms, enhancement of agricultural production, and generally increasing our health, comfort and well-being.

Unfortunately, there are also undesirable consequences associated with the use of these chemicals, particularly for some heavy metals and synthetic organic chemicals. Such materials, termed toxic substances, have the potential to fundamentally influence the character and environmental health of aquatic ecosystems, including the animal and plant communities contained within them. Many have also been shown to be hazardous to human health, via human consumption of aquatic organisms or other use of the water resource.

In spite of their widespread use, however, our knowledge of the human and environmental impacts of many chemicals remains grossly inadequate. We know very little about their movement, transformations, or ultimate environmental fate in aquatic ecosystems. In spite of this reality, however, there is every indication that the use of such chemical substances will increase in future years, in order to satisfy the growing requirements of increasing human population and development.

This guidebook, "Management of Toxic Substances in Lakes and Reservoirs", attempts to provide technical guidance to those concerned with the toxicology, environment fate, and modeling of toxic substances in these important water resources. It also provides guidance too individuals and agencies responsible for managing the quality and safety of lakes and reservoirs. It is hoped that both technical and non-technical audiences will find this guidebook useful in their daily work related to toxic pollution of these aquatic ecosystems.

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FOREWORD

Tatuo Kira

Nearly thirty-five years have already passed since the toxic contamination of aquatic ecosystems due to industrial wastes resulted in the first tragic events of *Minamata* and *itai-itai* diseases in Japan. We may also recall that Rachel Carson's *Silent Spring* was published just 30 years ago. Nevertheless, contamination from deleterious chemicals such as heavy metals and organochlorine compounds is still one of the most critical environmental problems in lakes, rivers and inland seas of the world. Even in developed countries, a number of water bodies still remain badly contaminated to the extent that local residents are strictly warned against carelessly eating fish or drinking water. During the course of the UNEP/ILEC Joint Survey on the State of World Lakes since 1987, we have been aware of the fact that the same is also the case with lakes in developing countries, but that reliable information is extremely limited in those countries. What we know might be but a small visible part of the huge hidden mass behind.

In addition to these so-called classical problems, the world is now facing a new type of toxic contamination by mutagenic chemicals, many of which are also carciogenic. In the short term, these substances are much less harmful than the contaminants involved in classical pollution-diseases, but in the longer term they are no less dangerous. Their effects tend to appear after a long period and are therefore probabilistic. The assessment and management of their risks offer various difficulties, not only in establishing a theoretical basis but also in consistency with the conventional ways of people's thinking and social life. We have as yet, made only a few steps towards the effective control of this new type of toxic pollution.

Guidelines for the management of toxic contamination that cover these aspects are urgently desired, but apparently very difficult to be concise and complete. This volume is a challenge to this hard task, reviewing diverse aspects of the problem from the ecotoxicological viewpoint and presenting basic concepts and management experiences based on several case studies. ILEC hopes that lake environment managers will find it useful and helpful for their work.

Many thanks are due to the editor, Professor Saburo Matsui, and all the contributors to this book for their effort and cooperation, and to the United Nations Environment Programme and Shiga Prefectural Government for their continued support.

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CHAPTER 1

INTRODUCTION

Saburo Matsui

1.1 SCOPE OF THE BOOK

Toxic management of lakes and reservoirs is aimed at the protection of human health and aquatic life from impacts caused by the release of toxic substances to surface waters. Lakes and reservoirs hold important freshwater ecosystems of the globe, in which a great number of species, including human beings, interact with each other. Special care must be taken when releasing toxicants into lakes and reservoirs because of the unique physical and chemical characteristics of confined water. Toxic substances are retained longer in both water and sediments than in flowing surface water, which increases the risk of exposure of toxicants in terms of concentration and duration to both aquatic organisms and humans who depend on drinking water and food from lakes and reservoirs.

This Guideline Book covers basic concepts of aquatic ecotoxicology, case studies of the Great Lakes and practical experiences developed for toxic substances management in the Ruhr River basin, Germany. The three chapters that follow this introductory chapter introduce basic concepts for readers who are not familiar with ecotoxicology. Chapter 2 describes general principles of toxicology which focuses on ecotoxicology on aquatic life with an emphasis on the uniqueness of the ecosystem of lakes and reservoirs. Chapter 3 describes the movement of toxic substances through bioaccumulation and deals with the important chemical factors involved in bioconcentration and bioaccumulation. The ecological structure of biomagnification are also emphasized and the Minamata and Itai-itai diseases are briefly introduced. Chapter 4 focuses on modelling of lake ecotoxicology, relating toxicant movement in lake ecosystems quantitatively so that readers can understand basic concepts of toxic management in terms of mass balance.

The remaining chapters deal with specific groups of toxic substances. Chapter 5 describes heavy metal and other inorganic toxic substances, in which the sources, movement and sinks of representative heavy metals and other inorganic substances are introduced with important points for their management. Chapter 6 describes organic pesticides in aquatic environments -- the Great Lakes studies in which detailed information on pollution from many prominent pesticides is clearly summarized with an emphasis on the importance of atmospheric migration of those pesticides over entire lakes. Chapter 7 describes other organic toxic substances with an overview of various organic pollutants in terms of sources, storage, transportation, use, fate, properties, and prevention policies are presented with an emphasis on common problems faced by developing countries with examples of PAHs, PCBs and chlorinated dioxins. Chapter 8 describes interesting practical experiences for the management of toxic substances in the Ruhr River basin, Germany, where the Ruhr River Association is responsible for managing the entire basin with respect to the quantity and quality of water of 14 reservoirs as well as the river itself. The experiences of monitoring and surveillance, and mass balance accounts of heavy metals, chlorinated hydrocarbons, AOX, PCBs, pesticides and ammonia are introduced. Control and abatement measures with legal and financial aspects are also described.

1.2 BASIC STAND TO MANAGE TOXIC SUBSTANCES IN AQUATIC ENVIRONMENTS

More than 9 million chemicals are listed on the Chemical Abstract Service's Registry of Chemicals in 1990, and the number of new chemicals is steadily increasing, although only an estimated 76,000 are in daily use. Some estimates of the total global number of species show about 27.7 million in existence (see Table 1.1). A substantial number of these species are aquatic, although often limited in their distribution. When comparing the number of chemicals and these aquatic species for toxics control, it is strikingly obvious that there is insufficient information on the toxicity of chemicals for each species. Moreover, our understanding of the toxicity of chemicals on human health in terms of environmental pollution is still very limited. Readers will understand that the subject of toxic substances management in aquatic ecosystems is both very difficult and complex.

Table 1.1 Summary of Plant and Animal Species Numbers (Kenega, 1987)

Taxonomic groupings	Approximate numbers of species
Plankton kingdom	
Algae, macrophytes (aquatic and terrestrial)	350,000
Animal kingdom	1,200,000
Vertebrates	37,790
Fishes	17,000
Birds	8,600
Reptiles	6,000
Mammals	4,300
Amphibians	1,500
Invertebrates	1,150,000

Toxicology is the study of the adverse effects of chemicals on living organisms by examining the nature of these adverse effects and assessing the probability of their occurrence. Toxicology can be further classified into the following areas; descriptive, mechanistic and regulatory.

Descriptive toxicology is concerned directly with appropriate toxicity tests in which experimental organisms are designed to yield information that can be used to evaluate the risk posed to humans and other species of organisms in the environment by exposure to specific chemicals.

Mechanistic toxicology is concerned with elucidation of the mechanisms by which chemicals exert their toxic effects on living organisms. Results of these studies help to develop more predictive tests useful in obtaining information for risk assessment.

Regulatory toxicology is responsible for deciding whether or not a chemical has a low enough risk to be marketed for its described purposes on the basis of data from descriptive toxicity tests. In general, food and drug administrative agencies are responsible for regulating drugs, cosmetics, food additives and agrochemicals, while environment protection agencies are responsible for regulating most other chemicals in establishing standards for the amount of chemicals permitted in ambient air, water, drinking water and soils. Environmental toxicology can be defined as the toxicology focusing on the study of the adverse effects of target chemicals on the entire ecosystem assessing the risk posed to both humans and other organisms by the chemicals.

Readers who wish to obtain further information on the basic science of toxicology are advised to consult relevant text books (for example, TOXICOLOGY, edited by J. Doul, C.D. Klaassenn and M.O. Amdur, second edition, Macmillan Publishing Co., Inc. New York, 1980). In this book, readers will learn of new ideas and case studies which are more oriented toward environmental toxicology of the ecosystems of lakes and reservoirs. In this book toxic substances are classified by conventional types of chemicals; heavy metals, pesticides, chlorinated organic substances etc., based upon the availability of information on environmental toxicology.

Management of toxic substances in the lake and reservoir environment consists of two parts; (1) risk assessment of target toxic substances in the specific lake and reservoir ecosystem; and (2) development of a control method of target toxic substances based upon the results of the assessment for the ecosystem. Risk assessment of the target chemicals firstly needs collection of basic information on the environmental toxicity provided by governmental agencies, universities and international supporting agencies such as the International Register of Potentially Toxic Chemicals (IRPTC - see Appendix for information on this organization). Commercial international information systems such as the Chemical Information System in the U.S.A. and the Environmental Chemicals Data and Information Network in the EC are also useful. With regard to information on the human cancer risk of chemicals, the International Agency for Research on Cancer (IARC) provides a series of monographs on evaluation of the carcinogenesis risk of chemicals to man.

As a first and simple step towards risk assessment, it can be said that a chemical compound which is likely to be a severe pollutant has the following characteristics; high toxicity potential; high dispersion tendency; persistence in the environment; bioaccumulation tendency; large production volume and large discharge into the environment. Industrial wastes of air, liquid and solid states, often contain toxic substances of the above characteristics so that careful treatment and disposal of toxic substances is essential for polluters to continue their production. Industrial polluters must consider the level of treatment and disposal of target toxic substances to meet the environmental standards set by regulatory agencies. Risk assessment is conducted to set up the appropriate environmental standards by the regulatory agencies.

Risk assessment of new chemicals, before commercial production, is conducted by the industrialized member countries of the Organization for Economic Cooperation and Development (OECD). One of the environmental activities of the OECD is to provide a guideline on "Chemical Testing Programme" and "Special Programme on the Control of Chemicals" under which new chemicals for the use of industrial purposes (except drugs, food additives and agrochemicals) are evaluated as to whether they are environmentally safe to put into commercial production. The OECD guidelines for the testing of chemicals is discussed in greater detail in Chapter 3.

The regulatory work of risk assessment of drugs, food additives, cosmetics and agrochemicals is traditionally carried out by individual countries. Drugs, food additives and cosmetics are usually only evaluated for risks to human health and not for environmental safety after disposal. Information on the fate of those types of chemicals in the environment is very limited. Further research is necessary to find appropriate methods of environmental risk assessment of drugs, food additives and cosmetics after use.

Pesticides have been regulated by agricultural agencies with traditional methods of risk assessment. However, over use and misuse of pesticides in many developed and developing countries have required the improvement of traditional risk assessment into more stringent methods and with greater orientation toward environmental safety. Problems inherent to agrochemicals are dealt with in Chapters 6 and 8.

The control of toxic substances requires the following stand points; (1) source identification and source control of target toxics; (2) fate and sinks determination for the mass balance of the target toxics; (3) a lake and river basin approach for source control of the target toxics. If toxic substances are discharged from point sources such as industrial wastewaters, municipal wastewaters and solid wastes landfill sites, the source identification is easier for control than other cases of non-point sources. If toxic substances migrate to the lake and reservoir environment through multiple routes including surface water, ground water, rain water and air pollution, the control of toxic substances is very difficult and requires comprehensive measures.

Management of toxic substances requires an institutional approach in which responsible local agencies must accumulate information on target toxics and practice source control of the toxics in the scope of the lake, reservoir or river basin concerned. The cooperation of national and state governments is also crucial in the control of toxic substances. Governments must support the activities of local agencies in order to build an information network and increase the capacity of toxic chemical analysis of local agencies. In order to implement effective source control of target toxics, it is necessary to set regulations by which responsible local agencies can obtain information on toxics inventory from factories, laboratories and hospitals and universities etc., which discharge toxic substances. Developing countries must make great efforts to increase the capacity of toxic management and they must be helped by developed countries to achieve this.

1.3 BASIC TERMINOLOGY OF AQUATIC TOXICOLOGY

The following key words are basic terms in the field of aquatic toxicology. Definitions of terms are mainly quoted from the Technical Support Document of the US EPA for Water Quality-based Toxics Control (1991).

ACUTE TOXICITY / CHRONIC TOXICITY - Toxic effects may be produced by acute / or chronic exposure to chemical agents. Acute toxicity is defined as toxicity caused by acute exposure including a single exposure or multiple exposure occurring within a short period. In aquatic toxicity tests, a toxic effect observed in 96 hours or less is considered acute. When referring to aquatic toxicology or human health, an acute effect is not always measured in terms of lethality. Chronic toxicity is defined as toxicity caused by chronic exposure that continues for a relatively long period of time, often one-tenth of the life span or more. Chronic is a relative term depending on the life span of the target organism.

LC/ NOEC/ LOEC/ EC - Lethal concentration is the concentration of a toxicant at which a certain percentage of the test organisms die, e.g. the LC_{10} or LC_{50}. An exposure duration is also included in the endpoint such as 24, 48, 72, or 96 hours (e.g. 96-hour LC_{50}). Commonly used chronic toxicity endpoints are the non observed effect concentration (NOEC), the lowest observed effect concentration (LOEC), and the effective concentration (EC). The NOEC is the highest concentration of toxicant to which the test organisms are exposed that caused no observable adverse effect. The effects measured may include sub-lethality or lethality. Sub-lethality means a stimulus below the level that causes death such as decreases in reproduction, fertilization, growth and abnormality. The effects also include survival from life cycle, partial life cycle, and early life stage tests with aquatic organisms. The LOEC is the lowest concentration of toxicant to which the test organisms are exposed that causes an observed effect. The EC is the toxicant concentration which would cause an adverse effect upon a certain percentage of the test organisms, (e.g. EC_{10} or EC_{50}).

ADDITIVITY / ANTAGONISM / SYNERGISM - Additivity is the characteristic property of a mixture of toxicants that exhibits a total toxic effect equal to the arithmetic sum of the effects of the individual toxicant. Antagonism is the characteristic property of a mixture of toxicants that exhibits a less-than-additive total toxic effect, while synergism is the characteristic property of a mixture of toxicants that exhibits a greater-than-additive total toxic effect.

BIOACCUMULATION / BIOCONCENTRATION - Bioaccumulation is the process by which a substance is taken up by an aquatic organism, both from water and through food, while bioconcentration is the process by which a substance is absorbed from water through gills or epithelial tissues and is concentrated in the body. Bioconcentration factor (BCF) can be defined as the ratio of a substance's concentration in tissue versus its concentration in water, in situations where the food chain is not exposed or contaminated. Bioaccumulation factor (BAF) can be also defined as the ratio of a substance's concentration in tissue versus its concentration in ambient water, in situations where the organism and the food chain are exposed.

BIOMAGNIFICATION - Biomagnification is the process by which a substance is taken up by an aquatic organism through food chains and thereby exhibits its increasing concentration in the organism related to its trophic status. The term "ecological magnification" is also sometimes used instead of biomagnification.

REFERENCES

Kenega, E.E., Methods for assessing the effects on non-human biota of mixtures of chemicals as applied to specific taxonomic representatives of individual or groups of species, in Vouk, V. B. *et al.*, edition: Methods for assessing the effects of mixtures of chemicals, SCOPE 30, SGOMSEC 3, John Wiley & Sons, 1987.

USEPA Technical Support Document for Water Quality-based Toxic Control, 1991.

CHAPTER 2

GENERAL PRINCIPLES OF TOXICOLOGY

Edwin E. Herricks

2.1 INTRODUCTION

The application of general principles of toxicology in lake and reservoir management requires an integrated testing program that will efficiently and effectively assess potential hazards and manage these hazards to minimize environmental impact. This integration of general toxicological principles and management is often accomplished by application of hazard evaluation procedures. A hazard evaluation applies the principles of toxicology, considering unique physical and chemical properties of the system receiving toxic discharges. Accepted hazard evaluation procedures (Mayer and Hamelink, 1977; Cairns, *et al.*, 1978; Bergman, *et al.*, 1986) require: 1) the determination of the sources and loading, 2) the location or fate of the material in the environment, 3) the expected concentration in the sediment, water, or organisms, and 4) the effect the material, at estimated environmental or exposure concentrations, will have on organisms and their interactions. Summarized as a "fate and effect" analysis, a hazard evaluation first requires development of a comprehensive understanding of the physical and chemical characteristics of the toxic substance followed by laboratory testing and field assessments to determine environmental or ecological effect. A review of the physical and chemical characteristics of different toxic substances is the focus of later chapters, this chapter will review the principles of toxicology and explore management of toxic substances through elements of the hazard evaluation process.

In the recently revised, standard text on toxicology, Amdur, *et al.* (1991) discuss the principles of toxicology in terms of the classification of toxic agents, characteristics of exposure, spectrum of undesired effects, interaction of chemicals, dose-response relationships, mechanisms of toxicity, descriptive tests, and predictive toxicology/risk assessments. Although this classification emphasizes human toxicology, these principles can be used to identify toxicological principles for lake and reservoir management. In lakes and reservoirs the classification of toxic agents can follow a number of schemes. In this paper, classification is based on effect type and responses expected in aquatic ecosystems. Characteristics of exposure are summarized based on the different physical and chemical dynamics of lakes and reservoirs. The spectrum of effects, interactions, concentration-response relationships and mechanisms of toxicity will be discussed in terms of the types of effects anticipated for both individual organisms and ecosystems. Descriptive testing will be discussed through a review of standard acute and chronic testing procedures, the use of microcosms or mesocosms, and the design and execution of field-based assessments. Predictive toxicology and risk determination will be addressed through a brief review of modeling for wasteload allocation and the state-of-the-art of environmental risk assessment.

2.2 CLASSIFICATION OF TOXIC AGENTS

Effect Type - The expected effect of a toxic substance will vary based on the concentration and the length of time a given concentration is maintained. High concentrations will normally produce an acute response. Low concentrations will produce a chronic response, requiring a long time period for the effect to develop. When toxic substance effect is evaluated in a toxicity test, duration is fixed to a specified time interval, and the concentration or dose is adjusted to produce either an acute or a chronic response. This relationship - a dose or concentration response curve - is illustrated in Figure 2.1.

The dose/concentration response curve can be separated into three areas where different management strategies must be employed. The first region includes those low dose levels where the response is uncertain, or where extremely long times are required for a response to develop. In this exposure range it is extremely difficult, if not impossible, to quantify and validate an effect. Effect determination is limited because the living systems being tested are inherently variable. This variability masks response to the toxicant. The major management challenges occur when toxic substance concentration/exposure events occur in this region of the dose response curve. Because response is indeterminate at these exposure levels two interpretations are possible that lead to vastly different management approaches. Note that the dotted lines in Figure 2.1 can be drawn to any point between the origin and the dose where a response is observed. If the line is extended to the origin, the assumption is made that any addition of a toxic substance will produce a response. If the line is drawn to any other point, the assumption is made that no response occurs until a "threshold" dose or concentration is reached. If the assumption is made that any increase in the toxic substance will produce an effect, the management strategy must completely eliminate the toxic substance from the environment. If a threshold of response is assumed, a safe discharge level can be identified, allowing release of the toxic substance with no damage. Unfortunately for management, both interpretations can be made from the same data, sparking controversy and confusing decision makers and the public.

In the second region of the dose/concentration response curve, a response is clearly related to a given dose or concentration of a toxic substance. The onset of an observable response defines a quantifiable threshold. Increasing dose or concentration produces a graded response with the severity of effect increasing with the dose or concentration. Managing toxic substances when a response is linked with a given concentration or dose is straightforward. Costs and benefits can be assessed and control strategies implemented to maintain toxic substance concentrations below an identified threshold.

In the final region of the curve, response is no longer graded and increasing dose produces no corresponding change in response. The occurrence of this region will depend on the response assessed and the design of the testing procedure. Under some conditions, this region of the curve may play an important role in management strategy. For example, if the intent is removal of a nuisance species (such as algae in a lake), complete removal may only be achieved only after large amounts of a control agent (toxic substance) has been used.

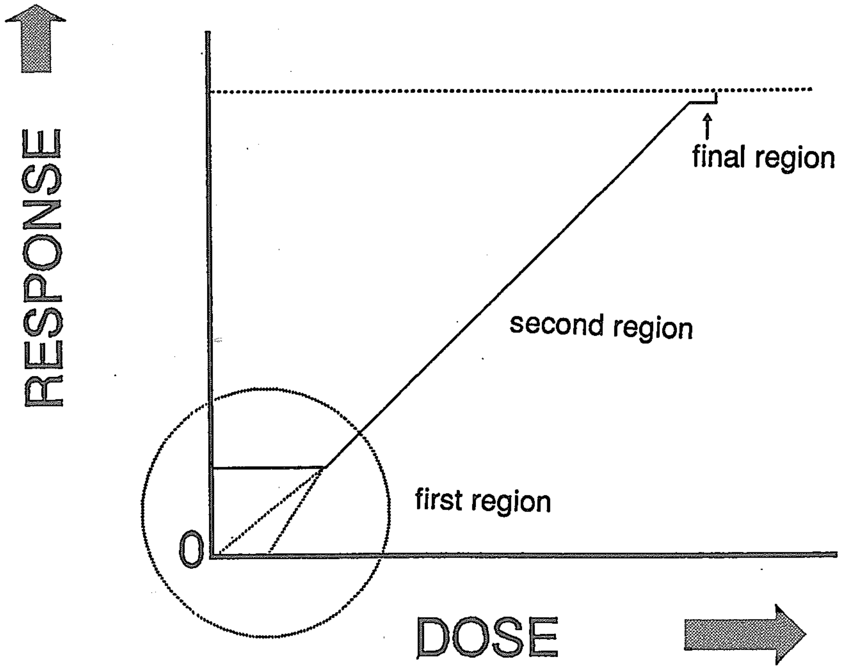


Fig. 2. 1 Dose or concentration response curve

Types of toxic effect can be related to different areas of the dose/concentration response curve. Acute effects are most commonly associated with the graded response region of the curve while chronic effects are associated with the region where variability often masks response. An acute effect will occur during a short time period (hours) and produce severe effect (death or impairment leading to death). In standard practice, acute toxicity is measured in terms of an LC_{50} (lethal concentration for 50% of the organisms tested) for time intervals of 24 to 96 hours. When effects other than lethality are measured in a toxicity test an effect concentration for 50% of the organisms tested (EC_{50}) is determined. Acute tests are valuable because they provide an important screening tool to determine a "magnitude of risk" for a toxic substance. The lower the dose or concentration needed to produce an acute response is indicative of the higher risk posed by that substance in the environment.

A chronic effect will be produced by a low concentration and a long exposure time. Chronic testing can use mortality as a response, but since is usually difficult to assess an increased incidence of experimental mortality from natural mortality, other response measures are used in chronic testing. Changes in fecundity, age/size relationships, or the presence of tumors (carcinogenicity), are common responses used in chronic toxicity testing. These responses are usually reported in relation to no observable effect levels (NOEL) of the toxicant, or a maximum acceptable toxicant concentrations (MATC) that are associated with an "acceptable" response. Chronic testing moves beyond screening toxic substances to more definitively identify responses to toxic substances.

Because acute tests are effective mainly as screening tools and chronic tests are expensive and time consuming, a number of tests for intermediate effects have been developed. These tests normally decrease the exposure concentration and extend the time of exposure beyond that required for acute response, or use sensitive life stages to predict chronic effect from a short term test. These tests produce sub lethal effects, below the level that causes death and/or cumulative, strength increased by successive addition (Sprague, 1970).

Response Types and Assessment Issues - Acute and chronic effects can be assessed for virtually any measurable response in a living system. When applying the principles of toxicology, a response is first identified, and then an appropriate test system is selected that will allow experimental evaluation of a dose/concentration response relationship. Test systems can range from simple biochemical assays to manipulation of ecosystems or ecosystem components.

In lake and reservoir management, an important criteria for test system selection is environmental realism. Some acute and chronic responses are most easily determined in a laboratory-based testing procedure (toxicity tests), but laboratory-based testing may or may not predict actual environmental impact. This "laboratory to field" extrapolation problem is a common limitation to the direct use of toxicity tests in lake and reservoir, or for that matter, any environmental management approach because all of the possible combinations of environmental conditions can not be tested. Although laboratory-based toxicity tests will never provide complete environmental realism, toxic substances can be tested under more "realistic" conditions by improving test designs to better simulate environmental conditions. This realistic testing approach begins with a comprehensive, environmental assessment to identify natural ranges of physical and chemical conditions, and characterize indigenous flora and fauna. While this approach increases realism it still falls short of providing realistic conditions because it is simply impossible to quantify and then control multiple environmental variables, test indigenous species that are not commonly cultured in a laboratory, and conduct the number of experiments necessary to meet statistical rigor within commonly encountered time or fiscal constraints.

To meet the need for realistic testing, field experiments, in addition to laboratory-based testing are required. A field experimental approach leaves environmental variation uncontrolled but controls the setting of the experiment. Field experimentation is common in lake and reservoir management with experiments ranging from the use of limnocorrales to whole lake manipulation or assessment of numerous lakes with a range of environmental conditions and toxicant loading. Although field experimentation allows testing under realistic conditions, study complexity, dollar costs and possible environmental damage limit the broad scale application in lake and reservoir management. A solution selects a combination of laboratory and field-based testing and assessments that provide different levels of realism under conditions that are progressively more realistic.

As noted above, selection of a response is the first step in assessing the effect of a toxic substance in a lake or reservoir. Table 2.1 provides a summary of response measures commonly selected for use in laboratory and field-based experimentation. When reviewing these response measures, the reader should understand that as test complexity, and associated environmental realism, increases, response selection will move from individual response measures to ecosystem response measures, requiring increasing attention to the abiotic environmental characteristics listed in the table.

The Effects of Toxic Substances in Lakes and Reservoirs - The addition of a toxic substance to a lake or reservoir can produce responses from any of the measures identified in Table 2.1. Acute effects, produced by high concentrations of a toxic substance, are easily observed and have direct links between the material concentration and response, which supports rapid impact assessment. Chronic effects, produced by low concentrations of toxic substances, are not as easily observed because responses to toxic substances is often indirect making confirmation of cause and effect, and impact assessment, difficult. Table 2.2 identifies responses that are commonly used to assess acute effects that are particularly applicable to lakes and reservoirs. Fortunately, toxic substances are seldom encountered in environmental concentrations that will produce an acute response. More often, the environmental concentration of toxic substances produces subtle alteration in the structure and/or function of lake and reservoir ecosystems. These alterations are often observed as a change in several related measurements that effect the general character of the ecosystem. Table 2.3 lists these integrative responses common in ecosystems.

Summary - A wide range of acute and chronic effects can be measured in the vast array of organisms available in nature. Since responses may be specific to a species, or even a population group in a species it is often prudent to select a test organism that is commonly used in laboratory analyses. Although site specific realism may be lost, quality assurance issues and the availability of species baseline data support this experimental approach. The actual selection of a test system, whether for laboratory-based or field-based experimentation should follow rigorous test system selection procedures (Herricks and Schaeffer, 1987).

Table 2.1 Response categories used in toxicity testing and field assessments in lake and reservoir management. (after Herricks and Schaeffer, 1987)

RESPONSES COMMONLY MEASURED IN INDIVIDUAL ORGANISMS

I	1.	Mortality/Lethality - death, cessation of all functions of a living organism
I	2.	Fitness - the individual's relative contribution of progeny to the population
I	3.	Disease - a destructive process in an organism with a specific cause
I	4.	Mutation - a change in the genetic make-up of an organism
I	5.	Reproduction - the capacity of an organism to produce progeny
I	6.	Physiology - the organic processes and phenomena of an organism
I	7.	Acclimation - the capacity of an individual to modify life functions within the range of fixed genetic capability
I	8.	Individual behavior - the response system of an organism

RESPONSES COMMONLY MEASURED FOR INDIVIDUAL ORGANISMS AND POPULATIONS

	9.	Intraspecific Behavior - social response systems between organisms of the same species
I,P		9.1 territorality - social pattern of space utilization
P		9.2 dominance - rank-ordered systems that determine individual access and priority to natural resources
I,P		9.3 reproductive - specific sets of behavior associated with reproduction
P	10.	Epidemiology - the pattern of disease in a population
P	11.	Genotypic variation - the characteristic variation of the genetic make-up of a population
P	12.	Phenotypic variation - the characteristic variation in the physical characteristics of a population
	13.	Reproduction - capacity of a population to sustain itself through the production of progeny by individual members of the population
P		13.1 age/size specific mortality -
P		13.2 age/size specific survivorship -
P		13.3 age/size specific fecundity -
	14.	Physiology - the processes, activities, and phenomena of living systems
I,P		14.1 metabolism
I,P		14.2 bioaccumulation
I,P		14.3 translocation
P	15.	Adaption - modification of genetic scope of a population through change in genetic make-up of individuals

Table 2.1 continued

RESPONSES COMMONLY MEASURED FOR COMMUNITIES OF ORGANISMS AND ECOSYSTEMS

	16.	Interspecific Behavior - response systems between species (limited in this analysis to competitive interactions)
I,P		16.1 predation - capture of live animals for food
I,P		16.2 competition - mutual utilization of a limited resource
	17.	Decomposition - the mineralization of fixed carbon compounds
P,C		17.1 biomass loss
P,C		17.2 total gas production
P,C		17.3 nutrient and mineral residuals
	18.	Production - the fixation of carbon
P,C		18.1 gross productivity - total production/area/time
P,C		18.2 biomass accumulation
C		18.3 total O_2 release
P,C&E	19.	Recovery - the process where an ecological system or system characteristic returns to a normal or usual state following disturbance or displacement
C,E	20.	Resilience - the degree, manner, and phase of restoration of initial structure and function of an ecological system following disturbance
C,E	21.	Resistance - the capacity of an ecological system or system characteristic to resist disturbance or displacement of structure and function
P,C	22.	Connectivity - description of all linkages between elements of an ecological system; quantification of permanent or continuing relationships between species
P	23.	Featured/Indicator species - a species indicative of community or ecological system condition or a species judged important based on economic or political criteria
P	24.	Keystone species - a species judged to play a role in maintenance of ecological system structure and/or function greater than would be expected from its numerical abundance
P	25.	Patterns of succession - the sequential establishment of species in an ecological system
	26.	Guild theory - the organization of species into groups of similar function, habitat, or process
P,C		26.1 composition -
C		26.2 relationships -
C		26.3 interactions -
C	27.	Species diversity - the distribution of individuals among a series of identifiably discrete units
P,C	28.	Vegetative structure - the physical dimensions of plant species assessed for area and height

MEASURES OF ABIOTIC ELEMENTS USED TO INTERPRET BIOLOGICAL RESPONSES

	29.	Soil mediation of chemical effects
		29.1 nutrient and mineral retention
		29.2 leaching processes
	30.	Cover/Habitat definition
		30.1 physiography
		30.2 structural diversity
		30.3 chemical composition

Measurement Units : I - individual, P - species/population, C - community, E - ecological system

Table 2.2 Responses commonly used to assess an acute response to a toxic substance

Mortality/Lethality	Measured as lethal concentration for 50% of organisms tested (LC_{50}) if a median tolerance (Tlm)
Disease	Measured as an effect concentration (typically for 50% of organisms tested - EC_{50}) as the onset of symptoms - often an indirect effect of exposure
Mutation	Measured as an effect concentration, commonly assessed with simple life forms (bacteria) but also observed in cellular change in higher organisms (SCE and various adducts)
Reproduction	Measured as a reduced rate, commonly assessed in lower organisms with rapid reproductive rates
Physiology	Measured as an effect concentration, numerous measurements possible for a wide range of organisms
Acclimation	Measured as an effect concentration, commonly measured in higher organisms supported by biochemical analysis of acclimatory response
Behavior	Measured as an effect concentration, can be assessed in terms of individuals and interactions between populations (e.g. predation)
Decomposition	Measured as an effect concentration that alters the rate
Production	Measured as an effect concentration that alters the rate.

Table 2.3 Integrative responses of impacts produced by toxic substances in ecosystems (after National Research Council, 1991)

Elemental Dynamics	inputs, internal transport, and losses of critical plants, animals, and biochemical compounds, including the flux of nutrients essential for primary production and secondary metabolism.
Energy Dynamics (physical)	energy exchange at geological and biological surfaces (e.g., isolation, sensible and latent heat fluxes, and transportation) and mixing processes (e.g. turbulence, convection, and advection).
Food Web (trophic dynamics)	the set of trophic relationships among species in a community. In its simplest form, the food web is an energy-flow diagram connecting each consumer to all species that it consumes. However, in its dynamic form, the concept also includes rates of consumption, preference of food items, and prey switching. A given food web may indicate which species are necessary resources for other species (e.g., a particular valued species), the amount of redundancy in community functions, and the degree to which particular consumers, termed "keystone" species may control the competitive processes among the species consumed.
Biodiversity	the number of taxa per unit area as represented by populations, guilds, or life forms, as well as the relative abundance of various taxa.
Critical Species	keystone, resource, and endangered species: keystone species are those that exert influences over other populations in their ecosystem out of proportion to their abundances; resource species are species that have energetic, economic, or aesthetic importance; endangered species are species in imminent danger of becoming extinct.
Genetic Diversity	genetic diversity represents the number and frequency of different genotypes within species.
Dispersal and Migration	movements of individuals within and between ecosystems that are crucial to the population's survival and the ecosystem's health, including colonization or dispersal between habitats as well as movements of individuals to different habitats for food, reproduction, overwintering, or protection from predators.
Natural disturbance	externally driven disturbances, unrelated to human activities, that have major impacts on ecosystem integrity by altering the species composition, trophic structure, or other important ecosystem developmental processes; these disturbances include wind storms, fires, and floods resulting from weather patterns; these disturbances are often essential to maintenance of certain ecosystems.
Ecosystem Development (successional processes)	developmental changes (successional stages) in species composition through time, mediated by biological-physical interrelationships, resulting in a defined ecosystem structure and function.

2.3 CHARACTERISTICS OF EXPOSURE

A major determinant of toxic substances effect in a lake or reservoir is the exposure concentration and the length of time that concentration is maintained. To assess this exposure/duration relationship in lakes or reservoirs it is important to consider the physical and chemical characteristics of the receiving system, and the nature and location of organisms present.

Chemical Characteristics - The fate of a chemical entering a lake or reservoir will be determined, in part, by the physico-chemical properties of the element or compound. The material's solubility, vapor pressure, and partition coefficients establish the phase concentration and residence time. Sorption-desorption, volatilization, chemical transformation due to redox reactions, hydrolysis, or photochemical degradation, and transformations due to metabolic activity of organisms in the lake or reservoir are specific processes that affect the concentration of a toxic substance at a given location.

Receiving System Physical and Chemical Characteristics - Lakes and reservoirs differ in dynamic character and will exhibit different characteristics of exposure. Table 2.4 lists common physical measurements made on lakes. With each physical parameter the primary process affecting toxic substances is identified and an anticipated effect on concentration is listed. The primary concern associated with the addition of toxic substances to lakes and reservoirs is the high potential for these materials to concentrate in the sediments, water column, or organisms. The potential for concentration is associated with both the chemical properties of the toxic substance and the hydrodynamics and water quality of the basin. Critical basin hydrodynamic properties include retention time, seasonal mixing (monomixis, dimixis, polymixis) and currents. Lakes will typically have long retention times with defined, and consistent, mixing characteristics and current patterns related to atmospheric phenomena (wind and pressure driven seiches). Reservoirs will often have short retention times with mixing controlled by both flow dynamics and thermal properties of the water column that may change rapidly. Currents in reservoirs are often of high magnitude, associated with low magnitude and dynamics.

Other physical characteristics of lakes and reservoirs, such as temperature, color, light penetration or transmissivity, produce conditions that may lead to the storage or transformation of chemicals. Temperature, in both lakes and reservoirs, may produce stratification that isolate toxic substances from areas of the water column or may contribute to the rate at which chemical or biological transformations of toxic substances occur. Temperature conditions and stratification will be more predictable in lakes than reservoirs. Water quality, particularly parameters related to light transmission or penetration will affect phototransformation rates and location. Some toxic substances may be photodegraded, reducing concentration, while others may be transformed or activated by sunlight increasing their hazard. It is expected that reservoirs will have higher suspended sediment concentrations, thus reducing phototransformation processes, although these processes will also be dependent on the trophic status of the lake or reservoir.

General basin characteristics, such as shoreline length or development, depth characteristics, and basin area or configuration can lead to localized conditions that affect the concentration of toxic substances. For example, shoreline length can be related to the potential for the partitioning materials to the sediment. Depth may be related to the potential for long term storage of toxic substances in profundal depths or the potential for bioconcentration due to the storage or accumulation of toxic substances in zones of high biological activity. Area, and in particular basin configuration in both lakes and reservoirs is associated with the potential for phototransformation and localized accumulation or storage of toxic materials.

Table 2.4 Physical Characteristics of Lakes and Reservoirs, Control Processes and Effects

Physical Characteristic	Primary Process or Processes That Control Toxic Substance Concentration	Effect Anticipated
Surface area	Photodegradation/activation	Concentration change, chemical transformation
Depth (maximum, average)	Photodegradation, Partitioning, Dilution, Storage	Concentration change, chemical transformation accumulation / bioconcentration
Volume	Dilution	Concentration change
Shoreline development, Shoreline length	Partitioning, Biotransformation, Storage	Concentration change, accumulation / bioconcentration
Temperature/Heat Budget	Chemical Reaction Rate, Biotransformation Rate	Concentration change, chemical transformation, accumulation / bioconcentration
Stratification/Mixing	Dilution, Transport, Isolation	Concentration change (seasonal cycles)
Retention Time	Dilution, Transport	Concentration change, distribution in basin
Currents	Dilution, Transport	Concentration change, distribution in basin
Color/Light Penetration	Photodegradation/activation	Concentration change, chemical transformation

In summary, the chemical properties of the toxic substance and the physical and chemical properties of the lake or reservoir will determine the fate of a toxic substance. A continuing interaction between the toxic substance and the receiving system may lead to storage or concentration of toxic substances, producing exposure conditions that may present a hazard. The dynamic character of reservoirs, specifically shorter retention times and greater transport potential, will lead to dilution and transport as a major mechanism of concentration change. The limited dynamics of lakes will lead to photo and biological transformations and partitioning as the major mechanisms of concentration change.

2.4 TESTING APPROACHES

Standard testing procedures for acute and chronic testing are readily available (Sprague, 1969; ASTM, 1980; APHA, 1985; USEPA; 1975; 1985; 1989). Algal assay procedures (USEPA, 1971) may be particularly well suited to the evaluation of toxic substances in lakes and reservoirs. For the purposes of this discussion, test system selection, and general procedures, equipment, and materials needed to conduct laboratory-based acute testing will be reviewed because of the common use of these procedures in initial management activities. In addition, since microcosms, and mesocosms are well suited to the testing of toxic substances effect on lakes and reservoirs, a number of procedures using these procedures will also be reviewed. A brief summary of field assessment requirements is provided to illustrate general requirements for data collection that can be used to improve test realism, and provide the foundation for field-based experimentation.

Acute Testing Facility and Containers - The facilities required for testing will vary with the size of the organisms being tested. The use of small invertebrates (e.g Daphnia or Cerodaphnia may be easily conducted on a bench top although additional laboratory space must be devoted to organism culture (USEPA, 1989) and temperature and photoperiod control in testing and culture are critical. The most common aquatic test organisms are fish. Fish culture requires a supply of non-contaminated water and sufficient space to hold fish while acclimating to test conditions. The test container used must be large enough to contain a minimum of 10 fish and not exceed loading limits (0.8 g/l for cold water species, 0.5 g/l for warmwater species). This loading will assure that a) the concentrations of dissolved oxygen and toxicant are not decreased below acceptable levels, b) the concentration of metabolic products does not increase above acceptable levels, and c) the organisms are not stressed because of crowding.

In static tests, containers should allow interchange with the atmosphere. Oxygen concentration in each test chamber should be between 60% and 100% saturation during the first 48h and between 40% and 100% after 48h. Test solutions may be gently aerated during static tests if the concentration of toxicant in the aerated test chamber at the end of the test is not more than 20% lower than in a comparable unaerated test chamber. When aeration is used, a simultaneous test without aeration should be conducted to determine if aeration affects test results. If flow-through testing is conducted, the flow rate should be set to provide a minimum of five replacements of 90% of the water volume in each test chamber in 24 hours, and the replacement rate should maintain needed dissolved oxygen concentrations.

The selection of test concentrations is dependent on the objective of the analysis. For example, if the objective of testing is to determine if toxicity is above or below a specified concentration, only a control and one concentration are necessary. Thirty organisms are needed for statistical confidence in results in this testing procedure. When toxicity is unknown, a range- finding or screening test is used to select concentrations. Range-finding tests use three to five widely spaced toxicant concentrations and a control, five organisms, and a duration of 8 to 24 hours. Screening tests are used with effluents. Five or ten organisms are exposed to a 100% effluent concentration for 24 hours. Once the range-finding or screening test is conducted, actual concentrations are selected. The highest concentration is selected based on the range-finding results. The concentration of toxicant in the remaining treatments should be at least 60% of the next higher concentration, and a minimum of five toxicant concentrations and a control should be used. However, if the toxicity is well known, it is possible to use fewer than six treatments or a dilution factor of greater than 60%. Table 2.5 provides a basis for selecting concentrations based on a logarithmic scale (APHA, 1981). Concentrations are selected by first determining the highest concentration (or percent) and then simply selecting concentrations that are close together or farther apart. The objective is the equal placement of concentrations on a logarithmic scale.

Table 2.5 Logarithmic scale for selecting toxicity test concentrations

HIGH CONCENTRATION				
10				8.7
			7.5	
				6.5
		5.6		
				4.9
			4.2	
				3.7
	3.2			
				2.8
			2.4	
				2.1
		1.8		
				1.55
			1.35	
				1.15
1.0				
LOW CONCENTRATION				

The species selected for toxicity testing should meet the following criteria: 1) be sensitive to the material or environmental factors, 2) have a wide geographical distribution and abundance and availability throughout the year, 3) have a known recreational, economic, or ecological importance, 4) have available culture methods for rearing and maintenance, and 5) be in good physical condition, free from parasites and diseases. Although good laboratory procedures can address criteria 4 and 5, criteria 1 through 3 may be unequally weighted in species selection based on testing objective. This species may be an indicator species (management orientation) or target species or group (ecosystem orientation).

An indicator species is a species that is commonly present or absent under specified environmental conditions and "indicates" environmental quality by its presence or absence. Indicator species have the following characteristics: 1) they accumulate various toxic substances, 2) they are common, 3) they have a broad geographic distribution, 4) they must be easily collected, 5) they must be of adequate size to permit resampling of tissue, 6) they must occur in the impact and unpolluted area, and 7) they must show correlation with environmental levels of the toxic substance.

A target species or group is, in a general sense, an ecological indicator that is maintained in a lake or reservoir. It is assumed that meeting the environmental requirements of the target species or group will protect the supporting ecosystem, affording general environmental protection. When selecting a target species or group, it should be recognized that each species will respond differently to a toxic substance, but groups or aggregates of species with similar characteristics may have similar responses to the same substance.

The most commonly used species aggregate is the community. Loosely defined, a community is composed of an interacting group of organisms in a specified habitat. Community measures are commonly used as surrogates to predict ecosystem response. Changes in both structural and functional measures of community condition are commonly made (Cairns, *et al.* 1982). Another species aggregation is the guild. Root (1967) identified a guild as "...species that exploit the same class of environmental resources in a similar way," leading to an aggregation of species based on resource utilization. In lakes and reservoirs, the aggregation of species depending of the same resource may provide a convenient base of extrapolation.

Microcosms, Mesocosms, and Field-Based Assessments - The acute responses listed in Table 2.3, and the majority of chronic test types depend on single species exposure. One method for increasing environmental realism is to experiment with multiple species. Microcosms, a contained portion of an ecosystem that is used in laboratory experimentation, are an initial step toward realistic testing. Microcosms generally have a total volume of less than 10 liters in volume with a defined species composition and are particularly well suited to the evaluation of toxic substance effect in lakes and reservoirs (Taub, 1985; Giesy and Allred, 1985). The defined nature of microcosms allows test replication and experimental control, but the limited array of species present and the lack of provision for some ecological processes (e.g. colonization) reduce the environmental realism of this testing approach.

Mesocosms are larger, multispecies experimental systems that are used to test ecosystem impacts from toxic substances. Mesocosms, with volumes of greater than 10 liters, include experimental ponds and in situ enclosures (often termed limnocorrals) that isolate a portion of the water column in a lake or reservoir (Touart and Slimak, 1989). Testing with mesocosms retain elements of controlled experiments, but not all environmental conditions are strictly controlled. Mesocosms provide added experimental realism for toxic substances analysis but are not easily replicated (Voshell, 1989). Mesocosms are particularly well suited to the evaluation of toxic substances effect in lakes and reservoirs. Many community and ecosystem measurements are easily made in mesocosms and the experimental design allows improved discrimination of effects when compared with an untreated reference system.

The foundation of all toxicity testing in lake and reservoir management is the field-based assessment that identifies physical and chemical conditions of the system and quantifies what organisms are present (community structure) and how they operate (community function) in the ecosystem. This data is used to design realistic testing procedures and support test result extrapolation to actual environmental effect. The basic design of field-based assessments includes single sample approaches, sequential sampling (over time or distance dimensions), and manipulations. In all field-based assessments, a reference (in time or location) that is unaffected by the toxic substance or manipulation is needed. The single sample approach provides a snapshot (specific time and location) of state and condition. Sequential samples, either in time or space, are used to identify changes in state or condition. Experimental manipulations allow a more direct determination of cause and effect in field experiments. (Note: field experiments use reference areas to determine change in state or condition and are not supported by true experimental controls).

The sampling design in field assessments should meet defined criteria to assure acceptable quality of the results. Herricks and Schaeffer (1986) propose a Study Design Assurance (SDA) process based on the criteria in Table 2.6. The integrative responses to toxic substances in ecosystems, Table 2.4, can be used as a general guide to measurement selection. Table 2.6 groups structural and functional measures that are commonly used to assess toxic substances effect in field assessments.

Table 2.6 Selection criteria for field assessment measurements (After Herricks and Schaeffer, 1985)

Criterion #1 -	The measurement must be biological or have proven relationships to biological/ecological effect in the system being managed.
Criterion #2 -	The measurement must be amenable to application at other trophic levels, reflect effects at other levels of the biological/ecological hierarchy, or provide an experimentally verified connection to other organisms or trophic levels.
Criterion #3 -	The measurement must be a good indicator, sensitive to the environmental conditions being monitored.
Criterion #4 -	The response range of the measurement must suitable for the intended application.
Criterion #5 -	The measurement must be reproducible and precise producing results within defined and acceptable limits.
Criterion #6 -	Variability of the measurement should be low. If variability is high, the distributional characteristics of the data must be known.

When analyzing community structure in field-based assessments it is necessary to define elements (species or an operational taxonomic unit (OTU) and species characteristics or relationships for analysis. The analysis of structure will typically include: 1) enumeration of numbers and kinds of organisms, 2) enumeration of abundance and biomass, 3) evaluation of population characteristics including size, biomass, and trophic status, 4) evaluation of community characteristics including change in composition and/or biomass, dominance changes, alterations in diversity, change in spatial structure, evidence of instability, and/or altered succession or recovery.

The fundamental functional characteristics of ecosystems are biomass production (ecological energetics), trophic or systems regulation, and nutrient cycling. The most promising measures of these functional characteristics include: 1) changes in primary productivity or respiration,

2) changes in energy flow, 3) changes in decomposition, 4) changes in material cycling, and 5) changes in internal regulatory processes.

Summary - A wide range of testing approaches are available to determine the effect of toxic substances on lakes and reservoirs. Unfortunately, the abundance of testing approaches makes it extremely difficult to select a single approach (or a test battery) that will meet all management needs. Some general guidance can be given. Simple toxicity tests with indigenous organisms, particularly tests that use species from multiple trophic levels known to occur in the lake or reservoir, can provide a screening-level assessment of toxic substance hazard. The next level of experimentation should consider use of standardized microcosms or mesocosms. Accompanying any experimental toxicity testing program should be a well-designed, field-based assessment to place test results in the context of the local environment.

2.5 APPLICATIONS OF TOXICOLOGY IN MANAGEMENT

The objective of the testing and analysis of toxic substance effect in lakes or reservoirs is to support either management or the implementation of control strategies that will minimize environmental impact and maintain the physical, chemical, and biological integrity of the system. The best, direct guidance on the management of toxic substances can be found in the extensive literature on hazard assessment (Dickson, *et al.*, 1979; Bergman, *et al.*, 1986) and the developing literature on risk assessment (Fishbein, 1980; O'Neill, *et al.*, 1982; Barnthouse and Suter, 1986; Hunsaker, *et al.*, 1989; Suter, 1990; Gunther and Pestemer, 1990; Lave, 1990). In the hazard and risk assessment process, toxicity testing is combined with fate and effect analysis, often supported by predictive modeling and field assessment activities. To provide an example management approach to toxic substances control applicable in lake and reservoir management, Table 2.7 provides risk assessment criteria based on acute and chronic toxicity testing, and Table 2.8 provides an example of the integration of toxicity analysis in a tier testing procedure.

To apply the criteria in Table 2.7, hazard evaluation procedures should be used. From an understanding of the physical and chemical properties of the toxic substance and an understanding of receiving system dynamics an estimated environmental concentration (EEC) can be determined. Laboratory or field-based testing produces LC_{50} or no observable effect levels (NOEL) for the toxic substance. Table 2.8 suggests that a progressive more complicated and definitive tier testing procedure should be followed. This tier testing begins with acute toxicity testing and simple fate models progressing through chronic studies and more complicated environmental fate models to field-based assessments and long term monitoring of the toxic substance in the environment.

2.6 CONCLUSIONS

The application of the principles of toxicology in lake and reservoir management requires a thorough understanding of the nature of the toxicant (classification of toxic agent) and the character of the receiving system (characteristics of exposure). Experimental analyses define effect relationships for individual organisms, populations, and communities using standard methods or standardized assessment procedures following SDA guidelines. The end result is the support of management and control to assure long-term maintenance of the physical, chemical and biological integrity of lake and reservoir ecosystems.

Table 2.7 U. S. Environmental Protection Agency guidance for assessing toxic substance risk for aquatic organisms (after Urban and Cook, 1986).

Regulatory Presumption	Acute Toxicity	Chronic Toxicity
Presumption of no risk	EEC < 1/10 LC_{50}	EEC < Chronic no effect level (NOEL)
Presumption of risk that may be mitigated by restricted use	1/10 $LC_{50} \leq$ EEC < 1/2 LC_{50} EEC $\geq$ 1/10 LC_{50}	Not Applicable
Presumption of unacceptable risk		
Non-endangered species	EEC $\geq$ 1/2 LC_{50}	EEC $\geq$ Chronic effect levels including reproductive effects
Endangered species	EEC > 1/20 LC_{50} or EEC > 1/10 LC_{10}	EEC $\geq$ Chronic effect levels including reproductive effects; also any adverse habitat modification

Table 2.8 Testing tiers proposed by the U.S. Environmental Protection Agency in aquatic ecosystem risk assessments (after Urban and Cook, 1986)

RULE	HAZARD	EXPOSURE
1	Acute toxicity (LC_{50}) Rainbow trout Bluegill sunfish Daphnia magna	Tier 1 Tabular model for direct application to water (EEC:lentic) [Toxicant use information - how, where when] [Nontarget organisms - what, how many, where, when]
2 2 3	Fish early life stage (MATC or NEL) Invertebrate life cycle (MATC or NEL) Fish biological concentration factor (BCF)	Tier 2 Simple runoff model (Modified tier 1 model) (EEC: lentic)
4	Fish full life cycle (MATC or NEL) Fathead minnow	Tier 3 Computer runoff and exposure models (ex. EXAMS) (EEC: lentic and lotic)
5	Fish and aquatic invertebrate populations effects in field Simulated actual field effects (aquatic organisms)	Tier 4 Field residue monitoring (lentic)

Decision Rules:

1. All chemical except indoor end-use products that are volatile or have manufacturing use registration
2. If chemical will occur in water and if : likely to be continuous or recurrent ; LC_{50} , 1.0 mg / L ; EEC $\geq$ 0.01 x LC_{50} ; EEC < 0.01 x LC_{50} but reproductive or cumulative effects indicated; or chemical is persistent.
3. If chemical will occur in water and if : EEC $\geq$ 0.1 x NEL in tests of (2) above and fish reproductive physiology may be affected.
4. If significant concentrations are likely in aquatic environment and may accumulate in aquatic organisms.
5. Case-by-case basis depending on results of previous tiers

REFERENCES

Amdur, M. O., J. Doull, C. D. Klaassen (*Eds.*). Toxicology: The Basic Science of Poisons Pergamon Press, New York. American Public Health Association. 1981. Standard methods for the examination of water and wastewater. 15th edition. American Public Health Association, Washington, D. C.

American Society for Testing and Materials 1980. Standard practices for conducting acute toxicity tests with fishes, macroinvertebrates, and amphibians. ASTM E 729-80. American Society for Testing and Materials, Philadelphia.

Barnthouse, L. W. and G. W. Suter, II. 1986. User's manual for ecological risk assessment. ORNL-6251. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Bergman, H. L., R. A. Kimerle, A. W. Maki. 1986. Environmental Hazard Assessment of Effluents. Pergamon Press, New York. 366 pp.

Cairns, J. Jr., K. L. Dickson, and A. W. Maki. 1978. Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM STP 657. American Society for Testing and Materials, Philadelphia. PA.

Cairns, J. Jr. 1982. Biological Monitoring in Water Pollution. Pergamon Press, New York

Dickson, K. L., A. W. Maki, and J. Cairns, Jr. 1979. Analyzing the Hazard Evaluation Process. Water Quality Section, American Fisheries Society, Washington, D. C. Fishbein, L. 1980. Overview of some aspects of quantitative risk assessment. J. Toxicol. and Environ. Health 6(5-6):1275-1296.

Giesy, J. P. and P. M. Allred. 1985. Replicability of aquatic multispecies test systems. In J. Cairns, Jr. (*Ed.*), Multispecies toxicity testing, Pergamon Press, New York. PP 187- 247.

Gunther, P. and W. Pestemer. 1990. Risk assessment for selected xenobiotics by bioassay methods with higher plants. Environ. Manage. 14(3):381-388.

Herricks, E. E. and D. J. Schaeffer. 1985. Can We Optimize Biomonitoring? Environ. Management 9(6):487-492.

Herricks, E. E. and D. J. Schaeffer. 1986. Selection of Test Systems to Evaluate the Effect of Contaminants on Ecological Systems" Civil Engineering Series, Environmental Engineering Series No. University of Illinois, Urbana, IL. Herricks, E. E. and D. J. Schaeffer. 1987. Selection of Test Systems for Ecological Analysis. Water Sci. and Tech. 19(11):47-54

Hunsaker, C. T., R. L. Grahm, G. W. Suter II, R. V. O'Neill, L. W. Barnthouse, and R. H. Gardner. 1990. Assessing Ecological Risk on a Regional Scale. Environ. Manage. 14(3):325-332.

Lave, L. B. 1990. Risk Analysis and Management. The Science of the Total Environment 99:235- 242.

Mayer, F. L. and J. L. Hamelink. 1977. Aquatic Toxicology and Hazard Evaluation. ASTM STP 634. American Society for Testing and Materials. Philadelphia, PA.

National Research Council. 1991. Opportunities in Applied Environmental Research and Development. National Academy Press, Washington, D. C.

O'Niell, R. V., R. H. Gardner, L. W. Barnthouse, G. W. Suter III, S. G. Hildebrand, and C. W. Gehrs. Ecosystem risk analysis: A new methodology. Environmental Toxicology and Chemistry 1:167- 177.

Root, R. B. 1967. The niche exploration pattern of the blue-gray gnatcatcher. Ecological Monographs. 37:317-350.

Sprague, J. B. 1969. Measurement of pollutant toxicity to fish - I. Bioassay methods for acute toxicity. Water Res. 3, 793-821.

Sprague, J. B. 1970. Measurement of pollutant toxicity to fish - III. Sublethal effects and "safe" concentrations. Water Res. 5, 245-266.

Suter, G. W. II. 1990. Endpoints for regional Ecological Risk Assessments. Environ. Manage. 14(1):9-23.

Taub, F. B. 1985. Toward interlaboratory (round-robin) testing of a standardized aquatic microcosm. In J. Cairns, Jr. (*Ed.*), Multi-species toxicity testing, Pergamon Press, New York. PP 165-186.

Touart, L. W. and M. W. Slimak. 1989. Mesocosm approach for assessing the ecological risk of pesticides. In Voshell, J. R. (*Ed.*), Using Mesocosms to Assess the Aquatic Ecological Risk of Pesticides: Theory and Practice. Entomological Soc. of Am., Misc. Publication 75. pp. 33-40.

United States Environmental Protection Agency. 1971. Algal assay procedures: Bottle Test. National Eutrophication Program. U. S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon, 82 pp. United States Environmental Protection Agency. 1975. Methods for acute toxicity tests with fish, macroinvertebrates, and amphibians. Environmental Research Laboratory, Duluth, Minnesota. EPA-600/4-79-019. United States Environmental Protection Agency. 1985. Methods for Measuring the acute toxicity of effluents to Freshwater and Marine Organisms. EPA/660/4-85-013.

United States Environmental Protection Agency. 1989. Short-Term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms, Second Edition. EPA/600/4-89/001.

Urban, D. J. and N. J. Cook. 1986. Hazard evaluation division, standard evaluation procedure: ecological risk assessment. EPA-540/09-88-035, U. S. Environmental Protection Agency, Washington, D. C.

Voshell, J. R. (*Ed.*). 1989. Using Mesocosms to Assess the Aquatic Ecological Risk of Pesticides: Theory and Practice. Entomological Soc. of Am., Misc. Publication 75. 88 pp.

CHAPTER 3

MOVEMENT OF TOXIC SUBSTANCES THROUGH BIOACCUMULATION

Saburo Matsui

3.1 INTRODUCTION

Toxic substances are subject to influence of environmental factors before exerting their effects on aquatic organisms. When organic toxic substances enter an aquatic ecosystem, they are subject to natural processes that result in their partition and dispersion among various components of the system, namely transport processes, and their chemical alteration into other substances, namely transformation. It can be said that their transportation and transformation is the sum of the following processes; volatilization, photolysis, hydrolysis, biological degradation, exchange with sediments, and dispersion. Conservative toxic substances such as inorganic heavy metals are not subject to the above mentioned transformation, while organic heavy metals such as organotins are. Volatility as characterized by vapor pressure, is very important in controlling certain types of toxic substances such as DDT, PCBs etc., which significantly migrate into lakes/reservoirs through the surface of the water. Aqueous solubility is also important not only in that it provides an upper limit to the extent of incorporation of the substances in the aquatic environments, but also indicates hydrophobicity and thus, the potential for transfer into lipid phases of aquatic organism.

The Henry's Law coefficient or air-water partition coefficient H is an indication of the likely partitioning behavior of the substances between the atmosphere and water bodies. When solubility S , the molar concentration in water at equilibrium with air of the substance, and vapor pressure P, the molar concentration in air at 1×10^5 Pa and 25°C data, are available, H can be obtained from

$$H = S/P \tag{3.1}$$

The H value is temperature dependent and increases generally as temperature increases. Table 3.1 provides equilibrium vapor pressures and Henry's Law coefficients of several chemicals (Southworth *et al.* 1982). DDT and PCBs are widespread atmospherically on a global scale, though their low equilibrium vapor pressures indicate that high pressure is not a requisite for atmospheric transport.

Table 3.1 Vapor Pressures and Henry's Law Coefficients for Several Environmental Contaminants at 25°C (after Southworth et al. 1982).

Substance	Vapor pressure, Pa	Henry's Law Coefficient, H*
Dimethyl phthalate	1.3	2×10^{-3}
Mercury	1.3×10^{-1}	5×10^{-1}
DDT	1.3×10^{-5}	2×10^{-3}
Atrazine	4.0×10^{-5}	1×10^{-7}
SO_2	Gas	2×10^{-4}**
Benz(a)pyrene	9.0×10^{-7}	1×10^{-5}
PCB (Aroclor)	1.0×10^{-2}	2×10^{-1}
CO_2	Gas	1.0

* Molar concentration ratio, gas-water at 1×10^5 Pa and25°C
**Include hydration, $SO_2 + H_2O \rightarrow \leftarrow H_2SO_3$

Photolysis takes place with chemical molecules which can absorb light energy. The photon energy rich molecules become fragile and are accelerated to breakdown. There is a detailed discussion of photolysis in Chapter 4. Hydrolysis of chemical molecules usually results in introduction of a hydroxyl radical (-OH) into the molecules in which it is clear that the reaction depends upon pH. Biological degradation includes microbial degradation, breakdown by photoautotrophs, and metabolic transformation by higher aquatic organisms. The information on those biological transformations by photoautotrophs and higher aquatic organisms is very limited.

Sorption of organic substances on or in sediments is also a very important phenomenon in the aquatic environment. The sediments can act as a sink for sorbed materials, removing them from water. Certain types of chemicals are retained in the sediments for a long period. However, other types of sorbed chemicals are often desorbed from the sediments afterwards. In this way, sorbed chemicals can become a source of pollution.

Dispersion or dilution is an important factor for toxic substances in the aquatic environment. In the past, mistakes were made in the choice of pollution control for toxic substances, which relied too heavily on the dispersion or dilution method for pollution control without understanding the biological magnification of the toxic substances in the aquatic ecosystems. This Chapter discusses the importance of biological factors for transmitting toxic substances in food chains.

3.2 SORPTION -- PARTITION BETWEEN WATER AND SEDIMENTS

Many toxic substances are retained in the sediments and afterwards released into the water phase so that aquatic toxicity usually lasts long. The tendency of migration of any chemical onto the sediments can be evaluated by the value of the distribution coefficient, Fs (see Chapter 4). The distribution coefficient is defined as:

$$Fs = C^*/To^* \tag{3.2}$$

where C^* is the concentration of a chemical sorbed (mg/g dry particulate) and To^* is concentration of the chemical in solution (mg/L). This expression is actually a simplification of the empirical Freundlich Adsorption Isotherm:

$$Fs = C^*/To^{*1/n} \tag{3.3}$$

in which n = 1. Such simplification is generally valid at the low concentration of suspended loadings typical of natural waters. If suspended matters increase in a water body, reduction of the dissolved concentration of the chemical due to sorption by the suspended particulates is described by the following equation:

$$f = 1/[Fs(c) + 1] \tag{3.4}$$

where f is the fraction of the total aqueous concentration present in dissolved form and c is the concentration of suspended particulates (g/L water).

Typical distribution coefficients for the sorption of several chemicals onto sediments or soils are shown in Table 3.2 (Southworth, *et al.* 1982)

Table 3.2 Distribution Coefficients, Kd, for Several Widespread Pollutants onto Sediments and Soils (after Southworth *et al.* 1982).

Substance	Kd	Sorbent
Lindane	3×10^2	Sediment
PCB (Aroclor 1254)	7×10^4	Sediment
Benze(a)pyrene	8×10^4	Sediment
2,4-D	3×10^0	Soil
Cs-137	$3.5\text{-}10 \times 10^3$	Sediment
Sr-90	$4\text{-}12 \times 10^1$	Sediment
DDT	1×10^5	Soil
Mirex	5×10^5	Sediment
Atrazine	$1\text{-}5 \times 10^0$	Soil
2,4,5-T	$0.3\text{-}3 \times 10^0$	Soil

The reader should understand from this table that organic chemicals having low aqueous solubility such as DDT, PCB and Mirex indicate considerable affinity for particulates, while more water soluble substances such as some types of herbicides, Atrazine, 2,4-D, 2,4,5-T, do not. Influence of suspended loadings at 10 - 50 mg/L, which is a typical concentration, shows that a chemical with the distribution coefficient Fs less than 1×10^4 would be less than 33% sorbed.

The most important sorption characteristics in determining Fs are size of particulates and organic content (see also Chapter 4). The smaller the particulate size and greater the organic content, the greater the distribution coefficients Fs are obtained. Environmental factors affecting Fs are those such as temperature, pH and salt concentration. Since sorption is generally exothermic (heat evolving), the distribution coefficients Fs usually increase with decreasing temperature. The pH of water is critical for compounds which ionize within the range of pH 5 - 10, and acts to a lesser degree to influence sorbent character. Dissolved salts are most important in saline lakes and brackish lagoons, where competing ions influence Fs. The reader can see that partition of toxic substances between dissolved and sorbed phases is vital to the evaluation of environmental fate via process rate studies; particularly certain processes such as volatilization that act only on the dissolved fraction, while sedimentation only on the sorbed fraction.

The direction of toxic chemicals movement, either into or out of sediments, is determined by the net magnitude of the coupled sorption - desorption rates. Sorption rates of chemicals from water can be expressed using a one-dimensional mass transfer coefficient similar to the approach used to describe gas exchange rates between liquid and gas phases. Uptake coefficients for movement from water to sediments of 0.1 -0.2 cm/hr were observed in still water, and increased up to 32 cm/hr in flowing water under laboratory conditions (Kudo, *et al.* 1971, 1974). This suggests that the uptake of chemicals with high sorptive affinity for sediments by previously uncontaminated sediments is initially limited by aqueous phase processes (delivery of the chemicals to the water sediment interface depending upon water turbulence, velocity, concentration, diffusion in sediments, etc.) Uptake may slow down under chronic exposure conditions and is mainly limited by diffusion into the sediments. Net movement from water into sediments probably has an insignificant effect on aqueous concentration because of the establishment of equilibrium conditions. Contrary to chronic conditions, rapid movement of chemicals into sediments would occur initially under acute exposure, but the overall mass of chemicals sequestered by bedded sediments would probably be quite small, due to the involvement of only the uppermost surface of sediments (< 1 mm) in the process.

Desorption of chemicals from bedded sediments may provide a significant input of toxicants to the water column (Kudo, *et al.*1971). The desorption coefficient of PCB is about 3×10^{-6} cm/hr which is large enough to produce aqueous concentrations in some systems that are near equilibrium (Halter, *et al.* 1977). Major factors affecting the desorption coefficients are water depth, water turnover time and the rates of removal processes such as microbial degradation and photolysis.

3.3 BIOACCUMULATION AND BIOCONCENTRATION -- PARTITION BETWEEN WATER AND ORGANISMS

The accumulation of toxic substances from the environment by aquatic organisms can be hazardous to both the organisms in question and other organisms ingesting them. The terms "bioaccumulation" and "bioconcentration" are distinguished in the following ways: bioaccumulation is the process by which a substance is taken up by an aquatic organism, both from water and through food, while bioconcentration is the process by which a substance is absorbed from water through gills or epithelial tissues and is concentrated in the body (USEPA Technical Support Document for Water Quality-based Toxic Control, 1991). Bioconcentration factor (BCF) can be defined as the ratio of a substance's concentration in tissue versus its concentration in water, in situations where the food chain is not exposed or contaminated. For nonmetabolized substances, it represents equilibrium partitioning between water and organisms. Bioaccumulation factor (BAF) can be also defined as the ratio of a substance's concentration in tissue versus its concentration in ambient water, in situations where the organism and the food chain are exposed.

Bioconcentration of organic and inorganic substances differs in that the uptake of organic substances by aquatic organisms is directly related to aqueous concentration, which is not so in the uptake of inorganic substances, due to homeostatic mechanisms and competitive uptake of other ions. This is specially important to see the bioconcentration of heavy metals in organisms. Bioaccumulation of an organic substance can be conceptualized as an equilibrium process in which elimination of the substance by metabolic and excretory processes counterbalances uptake from water, food, and in some cases, sediments. Rates of uptake and elimination can be estimated in laboratory studies and equilibrium concentrations of substances in test biota can be observed or calculated.

Many organic substances have low water solubility but high solubility in nonpolar solvents (lipophilicity). The partition coefficients as a measure of these properties is often determined in a system of n-Octanol/water. The relationship between water solubility and partition coefficient Kow is illustrated in Fig. 3.1 (Freed, *et al* 1977).

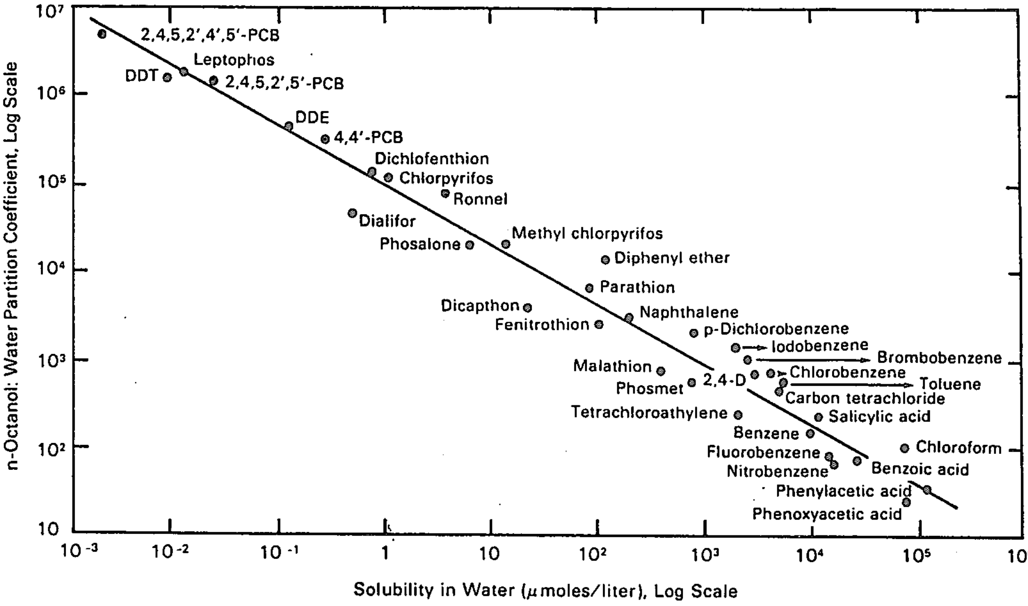


Fig. 3.1 Relationship between Water Solubility and n-Octanol/water Partition Coefficient (after Freed, *et al.*, 1977)

The importance of partitioning behavior of substances is primarily in the phenomenon of bioconcentration and bioaccumulation. Organisms in contact with water contaminated by a substance that has a high partition coefficient Kow will act as the nonploar phase of the binary system and accumulate it through a partitioning process. Bioconcentration and bioaccumulation factors (BCF and BAF) correlate well with the partition coefficient Kow, but other properties of substances must be taken into account, that is recalcitrance toward all types of degradation. Biological degradation including metabolic change and excretion play an important role in the bioaccumulation process.

In case of fishes, general observation of the relationship between the partition coefficient Kow and bioaccumulation factor BAF could indicate that any substance having Kow more than 10^4 shows BCF more than 500. Such a substance could be potentially very toxic to fishes. Substances with Kow between 10^2 - 10^4 may show BAF between 10 - 500, and may indicate hazardous effects on fishes depending on the toxic property of the substances. Substances with low Kow values less than 10^2 have lower BAF of less than 10 (Bro-Rasmussen, *et al.* 1984). The reader should see Chapter 4 for an estimation of the relationship between the partition coefficient Kow and BCF, BAF.

Bioaccumulation of inorganic substances is quite different from organic substances. Bioaccumulation factors of several important elements with different sea organisms are summarized in Table 3.3. The reader should also see Chapter 5 to gain a further understanding of heavy metal pollution.

Table 3.3 Bioconcentration Factors (BCF) and Bioaccumulation Factors (BAF) of Elements for Sea Organisms (after Thompson, *et al.* 1972).

	ALGAE, BCF	
Element	Bentohs	Plankton (phytoplankton, gulfweed, etc.)
Ag	100 - 1,000	<100 - 220
Cd	11 - 20	<350 -6,000
Ce	100 - 3,300	2,000 -4,500
Co	15 - 740	75 -1,000
Cr	100 - 500	<70 - 600
Cs	16 - 50	16 - 22
Fe	1,000 - 5x10^3	750 - 7x10^4
Hg	10 - 30	
I	160 - 10^5	
Mo	10 - 200	- 17
Mn	20 - 2x10^4	<300 -7,000
Ni	50 - 1,000	25 - 300
Pb	8,000 - 2x10^4	<1,000 - 3x10^6
Ru	<200 - 1,200	<200
Sr	0.1 - 90	0.9 - 54
Ti	200 - 3x10^4	600 - 10^4
Zn	80 - 3,000	200 -1,300
Zr	200 - 3,000	<1,000 - 2x10^4

	HERBIVORE, BAF	
Element	Plankton	Shellfish
Ag	<100	330 - $2x10^4$
Cd	<80 - 10^5	10^5 - $2x10^6$
Ce		40 - 300
Co	<110 - 10^4	24 - 260
Cr	<15 - 10^4	$6x10^4$ - $3x10^5$
Cs	6 - 15	3 - 15
Fe	440 - $6x10^4$	$7x10^4$ - $3x10^5$
Hg		5,000 - 10^4
I		40 - 70
Mo	2 - 175	30 - 90
Mn	21 - 4,000	3,000 - $6x10^6$
Ni	2 - 1,000	4,000 - 10^4
Pb	3,000 - $2x10^6$	39 -5,000
Ru	<10 - 6,000	1 -3,000
Sr	1 - 85	- 50
Ti	28 - $3x10^4$	
Zn	125 - 500	1,400 - 10^5
Zr	360 - $3x10^4$	8 - 36

	CARNIVORE, BAF		
Element	Plankton	Fishes	Squid
Ag	<45 - 900		900 - 3,000
Cd	<300 - 10^4	10^3 - 10^5	2,800
Ce		5 - 12	
Co	<70 - 1,300	28 - 560	<200 - $5x10^4$
Cr	<55 - 3,900	3 - 30	<70
Cs		10 - 100	
Fe	3,000 - $3x10^4$	400 -3,000	$7x10^4$ - $3x10^5$
Hg		1,000 -5,000	
I		10	
Mo	<2 - 14	- 200	<10
Mn	270 - 1,600	95 - 10^5	1,000
Ni	17 - 90		30 - 80
Pb	200 - $6x10^4$	5 - 10^4	100 - $2x10^5$
Ru	<160 - 2,400	10 <	<400 - 2,100
Sr	1.2 - 10	0.03 - 20	0.9 - 1.2
Ti	110 - $2x10^4$		300 - 3,000
Zn	- 50	280 - $2x10^4$	2,500
Zr	<800 - $4x10^4$	5	$2x10^4$

3.4 BIOMAGNIFICATION -- CONCENTRATION PROCESS THROUGH FOOD CHAINS

Bioaccumulation of substances through food chains exhibits increasing concentration in organisms related to their trophic status. The first evidence of biomagnification in wildlife was introduced by Rachel Carson in her book "Silent Spring", indicating that the mortality of American robins was linked to DDT in earthworms. Biomagnification highly depends upon toxicokinetics, that is the metabolic rate and excretion rate of a toxic substance in organisms. Since there is a tendency of biomagnification of toxic substances, species of organisms in higher trophic levels such as predatory water birds and insectivorous birds are potentially at high risk. However, persistent substances such as organochlorine pesticides do not universally increase along food chains, and the hazardous effect depends on both the species and the toxic chemical due to different toxicokinetics.

There are, in general, marked differences in the rate of toxic substances metabolism by vertebrates; small vertebrates > large vertebrates; omnivores and herbivores > predators; and mammals > birds > fish (Walker, 1980).

Human beings are also one of the species of organisms at the highest trophic level. Depending upon food habits, a certain group of people in regions where a toxic chemical is disposed of into the environment, may become a high risk group. The cases of Minamata disease and Itai-itai disease are typical examples.

Biomagnification of toxic substances may be influenced by the level of eutrophication of the aquatic ecosystems. According to the concept of biomass pyramids of aquatic ecosystems, there are three classified typical ecosystems (Odum E. P. 1959). When a toxic substance such as a heavy metal is released into the shallow water ecosystem, uptake of the toxicant by the producer takes place first. Due to the high level of eutrophication, a great amount of the toxicant is preserved in the bio-mass of producers. Compared to the producer, the biomass of herbivores is relatively small because of poorer ecological efficiency of biomass conversion, and the amount of toxicant held in the herbivores reduces significantly. Similarly the biomass of carnivores and top carnivores reduces in the ecosystem with decreased amount of toxicants held in the higher trophic levels. Contrary to the eutrophicated ecosystem, open water or the deep sea ecosystem has quite an opposite structure of biomass pyramids, where the biomass of the producer is less than that of the herbivores and carnivores indicating a high ecological efficiency of conversion of biomass. A greater amount of toxicant is held in the higher trophic levels than phytoplankton.

Mercury concentration of tuna fish in the ocean is generally observed to be very high compared to that of other fishes in shore lines and bay areas where the industrial release of mercury is detected to be high. Biological dilution of toxic substances by phytoplankton in the eutrophicated ecosystems should be taken into consideration. Toxic control of lakes and reservoirs requires understanding of the ecological structure.

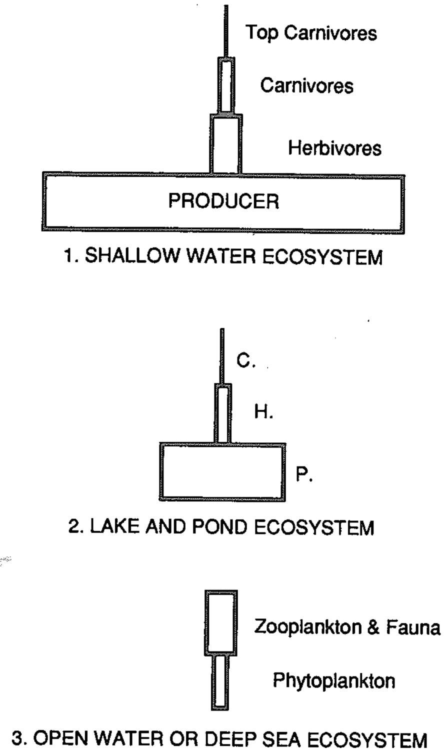


Fig. 3.2 Biomass Pyramids of Aquatic Ecosystems (after Odum, 1959)

3.5 THE MINAMATA DISEASE

Among numerous water pollution events in the past, the Minamata disease and Itai-itai disease cases are two of the most tragic lessons which human beings must not repeat again. Minamata disease and Itai-itai disease occurred in Japan during the 1940s and 1960s side by side with the rapid industrialization of the country. Minamata disease was associated with both methylmercury and inorganic mercury, though methylmercury is more causative. It was converted incidentally from catalytic inorganic mercury in the process of synthesis of acetaldehyde and vinyl chloride from acetylene in the Minamata Factory of Chisso Company, Ltd. (Irukayama, et.al. 1961, 1962-a, 1962-b, 1969). Both methyl and inorganic mercury were carelessly discharged, over a decade, in the industrial effluent into Minamata Bay connected to the Yatsushiro Inland Sea which has a poor exchange of water with the Pacific Ocean in the vicinity of Kyushu Island in the western part of Japan. Methyl and inorganic mercury were accumulated in various fishes and shellfishes through food chains and then magnified in the body of the group of people who ingested those contaminated fishes and shellfishes at a higher rate of consumption than other groups of people who lived in the surrounding areas of the Yatsushiro Inland Sea. Fishermen and their family members in the Yatsushiro Inland Sea areas were the highest risk group in the case of Minamata disease. Methylmercury mainly damages the central nervous system, while inorganic mercury exerts, in addition, toxicity to kidney and other organs. The main symptoms of the disease is cerebellar ataxia, concentric constriction of visual fields, dysarthria etc., (Tokuomi, 1968); congenital cases are accompanied by disturbance of physical and mental development (Harada, 1968). By 1987, the Japanese Government identified 1,742 patients as victims of Minamata disease. The number of potential patients is estimated to be more than 5,000. Besides human beings, cats and rats that fed on the fish or shellfish from the bay developed similar symptoms and findings as observed in the human patients of the disease.

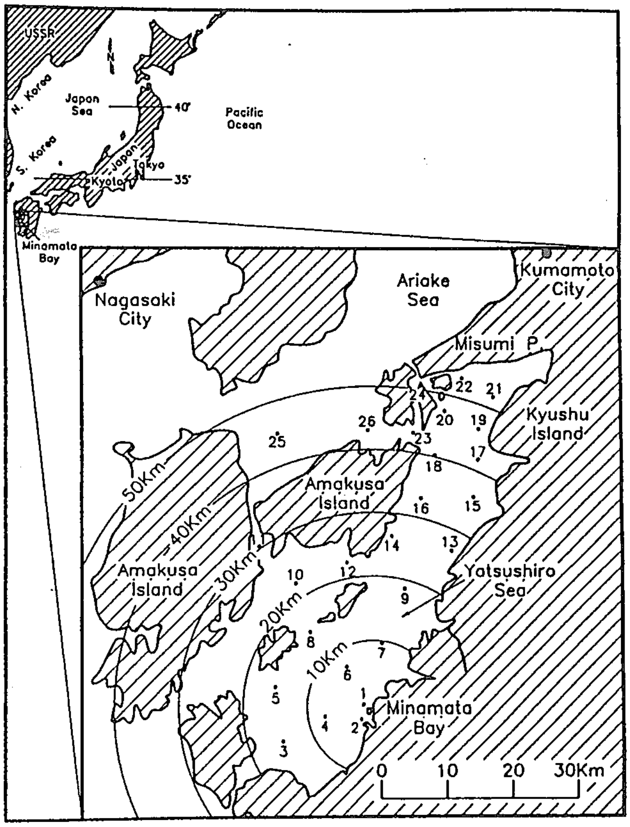


Fig. 3.3 Minamata Bay (after Kudo, *et al.* 1991)

The Minamata Factory of Chisso Company reported in 1959 that the mercury concentration of their industrial wastewater from the vinyl chloride plant was 0.1 mg/L and that from the acetaldehyde plant was usually about 20 mg/L. Mercury content in the surface sediments of Minamata Bay varied from 8 to 908 as Hg mg/kg dry weight. At one point in the bay, the vertical changes of mercury content were 160 Hg mg/kg wet weight at surface and 0 Hg mg/kg wet weight at 3.68 m below the surface. Mercury compounds in the sediments were mostly inorganic such as mercury sulfide and oxide, and the highest concentration of methylmercury was 0.015 mg Hg/Kg wet weight (Fujiki *et al.* 1973, 1977).

Mercury contamination of fishes is often observed when mercury content in the sediments of a water area exceeds several tens of mg/Kg over a wide area. The concentration of mercury in fish and shellfish from Minamata Bay and the neighboring seashore was very high in 1958; shellfish *Hormomya mutabilis* 108 mg/kg dry weight; shellfish *Venus japonica* 179 mg/kg dry weight; and fish *Nibea schlegeli* 15 mg/kg wet weight. The mercury concentration in shellfishes and fishes decreased significantly after 1968 when production of acetaldehyde and vinyl chloride was stopped at the factory. In 1971, fishes from the inner part of the bay contained 0.1 - 1.0 mg Hg/kg wet weight of total mercury and 0.062 -0.42 mg Hg/kg wet weight of methylmercury. There were 87 species of fish from the bay with total mercury concentration 0.01 -1.74 mg Hg/kg and 16 species containing over 0.4 mg Hg/kg of total mercury in 1989. The Ministry of Health and Welfare of Japan has set the provisional control value of total mercury in fishes at 0.4 mg Hg/kg wet weight in 1973.

The total amount of mercury deposited in the bay was estimated to be 150 tons. Mercury in the sediments has been dispersing to the Yatsushiro Inland Sea from Minamata Bay. The Japanese Government initiated, in 1984, a mercury decontamination project, vacuuming the contaminated sediments into a sealed area in Minamata Bay, creating a reclaimed land mass of 582,000 m^3. The initiation of the artificial decontamination work (costing over US $500 million) drastically reduced its contamination in the sediments. According to a prediction of the trend of decreasing contamination of Hg in the sediments of Minamata Bay, the sediments will be cleared up and restored to the background level by the year 2011 (Kudo, *et al.* 1991).

3.6 THE ITAI-ITAI DISEASE

Itai-itai disease is associated with cadmium, although the causative relationship between inorganic cadmium and the disease is not as straightforward as the case of Minamata disease with inorganic mercury and methylmercury. However, cadmium is the major causative factor of Itai-itai disease (Ishizaki, A. et.al. 1968). Along with the activities of the Mitsui Mining and Smelting Company for production of zinc, lead, silver and gold, cadmium was discharged in the industrial effluents to the Jinzu River in the central part of Japan, where water was utilized in the downstream areas for irrigation of paddy fields. Cadmium was concentrated in the grains of rice cultivated in the areas. The farmers in the areas consumed the rice contaminated by cadmium over several decades. Cadmium caused renal tubular dysfunction and osteomalacia with osteoporosis (Aoshima, K. *et al.* 1988a, 1988b). The distinct symptom of the disease is severe bone pain, thus the name "itai-itai" words meaning "it hurts, it hurts" in Japanese. Women patients who bore children, suffered more bone pain.

Although a large number of victims are thought to have existed in the period 1920 to 1950, official recognition of the disease did not start until 1967. The number of victims who died from symptoms like Itai-itai disease were surveyed to be 396 in total (305 female and 91 male) for 1,426 households in the paddy fields in the polluted areas (Kasuya, *et al.*, 1991).

Total cadmium discharged up until 1977 was estimated to be more than 3,000 tons (Kurachi, *et al.* 1980). The paddy fields irrigated by the cadmium contaminated Jinzu River showed contamination of cadmium in soils. About 90% of the surface of the soils showed more than 0.5 mg Cd/kg and about 4% showed more than 3 mg Cd/kg (Yanagisawa, *et al.* 1984). Rice harvested in the cadmium paddy fields showed cadmium concentration more than 0.4 mg Cd/kg unpolished and sometimes more than 1.0 mg Cd/kg unpolished (Yanagihara, *et al.* 1984). The Japanese Government decided to ban cultivating paddy fields which produce rice containing more than 1.0 mg Cd/kg unpolished. The Government advises against eating rice containing more than 0.4 cadmium.

The main exposure route of cadmium to the victims was consumption of contaminated rice which was cultivated by family members of the victims. The *Japonica* type of rice requires careful water control during cultivation period such as filling and drying up water in the paddy fields. During the filling period, the soil of the paddy fields is in a reduced condition and cadmium fixes to soil. When the water is drained, rice takes cadmium from the soil through its roots under oxidation condition. The relationship between the cadmium concentration of rice grain grown in the polluted fields and that of soils of polluted paddy fields was not in good correlation. Because of that, designation of polluted paddy fields was decided based upon cadmium concentration in the rice more than 1.0 mg Cd/kg unpolished grain which was cultivated in the fields. Cadmium concentration of the soils did not directly indicate cadmium contamination of the rice. The restoration work of the contaminated paddy fields has been carried out for about 50% of polluted areas (about 200ha) in 1991. The top 30cm of soil was mostly contaminated by cadmium. This top soil was placed deep into the bottom of the fields and covered with new top soil.

Cadmium in the sediments of the Jinzu River has remained and after floods, is discharged into the down reach in the form of suspended matters. Restoration of the bottom sediments of the river is very difficult.

Both the cases of Minamata disease and Itai-itai disease show typical human sacrifices caused by industrial water pollution upon biological magnification or the food chain mechanisms. When water pollution of toxic contaminants is considered only for the safety of drinking purposes, it obviously leads to dangerous situations.

3.7 OECD GUIDELINES FOR TESTING NEW CHEMICALS

Although OECD guidelines for testing new chemicals are accepted by 24 industrialized countries, other countries including developing countries need to pay attention to the content of the testing. As shown in Table 3.4, the guidelines cover four major categories of testing; (1) physical-chemical properties; (2) effects on biotic systems; (3) degradation and accumulation; and (4) health effects. The total test number of items amount to 85 different tests including accumulation tests of fish. Difficulties remain in this test system for evaluating effects of new toxicants on the ecosystems. In order to evaluate toxic effects on the aquatic ecosystems, three different trophic levels of organisms are selected for surrogates such as algae, daphnia and fish. The endpoints usually evaluated in ecotoxicological tests are mortality and behavior of fish, reproduction of daphnia, and growth of algae.

Table 3.4 OECD Guidelines for testing of new chemicals.

PHYSICAL-CHEMICAL PROPERTIES

101	UV-VIS Absorption Spectra
102	Melting point/Melting range
103	Boiling Point/Boiling Range
104	Vapour Pressure Curve
105	Water Solubility
106	Adsorption/Desorption
107	Partition Coefficient (n-octanol/water)
108	Complex Formation Ability in water
109	Density of Liquids and Solids
110	Particle Size Distribution/Fibre Length and Diameter Distributions
111	Hydrolysis as a Function of pH
112	Dissociation Constants in Water
113	Screening Test for Thermal Stability and Stability in Air
114	Viscosity of Liquids
115	Surface Tension of Aqueous Solutions
116	Fat Solubility of Soil and Liquid Substances
117	Partition Coefficient (n-octanol/water), HPLC Method

EFFECTS ON BIOTIC SYSTEMS

201	Alga, Growth Inhibition Test
202	Daphnia sp. Acute Immobilisation Test and Reproduction Test
203	Fish, Acute Toxicity Test
204	Fish, Prolonged Toxicity Test: 14-day Study
205	Avian Dietary Toxicity Test
206	Avian Reproduction Test
207	Earthworm, Acute Toxicity Tests
208	Terrestrial Plants, Growth Test
209	Activated Sludge, Respiration Inhibition Test

DEGRADATION AND ACCUMULATION

READY BIODEGRADABILITY

301	A Modified AFNOR Test
302	B Modified Sturm Test
303	C Modified MITI Test (I)
304	D Closed Bottle Test
305	E Modified OECD Screening Test

INHERENT BIODEGRADABILITY

302	A Modified SCAS Test
302	B Modified Zahn-Wellens Test
302	C Modified MITI Test (II)

SIMULATION TEST

303	A Aerobic Sewage Treatment: Coupled Units Test

BIODEGRADABILITY IN SOIL

304	A Inherent Biodegradability Test in Soil

BIOACCUMULATION

305	A Sequential Static Fish Test
305	B Semi-static Fish Test
305	C Degree of Bioconcentration in Fish
305	D Static Fish Test
305	E Flow-through Fish Test

HEALTH EFFECTS

SHORT-TERM TOXICITY

401	Acute Oral Toxicity
402	Acute Dermal Toxicity
403	Acute Inhalation Toxicity
404	Acute Dermal Irritation/Corrosion
405	Acute Eye Irritation/Corrosion
406	Skin Sensitisation
407	Repeated Dose Oral Toxicity-Rodent: 28/14-day
408	Subchronic Oral Toxicity-Rodent: 90-day
409	Subchronic Oral Toxicity-Non-rodent: 90-day
410	Repeated Dose Dermal Toxicity: 28/14-day
411	Subchronic Dermal Toxicity: 90-day
412	Repeated Dose Inhalation Toxicity: 28/14-day
413	Subchronic Inhalation Toxicity: 90-day
414	Teratogenicity
415	One-generation Reproduction Toxicity
416	Two-generation Reproduction Toxicity
417	Toxicokinetics
418	Acute Delayed Neurotoxicity of Organophosphorus Substances
419	Subchronic Delayed Neurotoxicity of Organophosphorus Substances: 90-day

LONG-TERM TOXICICOLOGY

451	Carcinogenicity Studies
452	Chronic Toxicity Studies
453	Combined Chronic Toxicity/Carcinogenicity Studies

GENETIC TOXICOLOGY

471	Salmnonella typhimurium, Reverse Mutation Assay
472	Escherichia coli, Reverse Mutation Assay
473	In vitro Mammalian Cytogenetic Test
474	Micronucleus Test
475	In vivo Mammalian Bone Marrow Cytogenetic Test - Chromosomal Analysis
476	In vitro Mammalian Cell Gene Mutation Tests
477	Sex-linked Recessive Lethal Test in Drosophila melanogaster
478	Rodent Dominant Lethal Test
479	In vitro Sister Chromatid Exchange Assay in Mammalian Cells
480	Saccharomyces cervisiae, Gene Mutation Assay
481	Saccharomyces cervisiae, Mitotic Recombination Assay
482	DNA Damage and Repair, Unscheduled DNA Synthesis in Mammalian Cells in vitro
483	Mammalian Germ Cell Cytogenetic Assay
484	Mouse Spot Test
485	Mouse Heritable Translocation Assay

REFERENCES

Aoshima, K. Iwata, K. and Kasuya, M., Environmental exposure to cadmium and effects on human health, Part I. Renal tubular function in inhabitants of the cadmium-polluted Jinzu River basin in Toyama Prefecture. Japan J. Hyg., 43,864-871, 1988a

Aoshima, K. Iwata, K. and Kasuya, M., Environmental exposure to cadmium and effects on human health, Part II. Bone and mineral metabolism in inhabitants of the cadmium-polluted Jinzu River basin in Toyama Prefecture. Japan J. Hyg., 43, 949-955, 1988b

Bro-Rasmussen, F., and Christiansen, K., Hazard Assessment - A summary of analysis and integrated evaluation of exposure and potential effects from toxic environmental chemicals. Ecological Modeling, 22:67-84. 1983/84

Freed,V.H., Chiou, C.T., and Hague, R., Chemodynamics-transport and behavior of chemicals in the environment--a problem in the environmental health. Environ. Health Perspect., 20:55-7-.1977

Fujiki, M. and Tajima, S., The pollution of Minamata May and the neighboring sea by factory waste water containing mercury. New Methods in Environmental Chemistry and Toxicology, F. Coulston, F. Korte and M. Goto (*Eds.*). International Academic Printing Co., Tokyo, pp217-229, 1973

Fujiki, M., Hirota, R. and Yamaguchi, S., The mechanism of methylmercury accumulation in fish. Ecological Research Series EPA-600/3-77-083, pp89-95, 1977

Halter, M. T., and Johnson, H. E., A model system to study the desorption and biological availability of PCB in hydrosoils. pp.178-195. In Aquatic Toxicology and Hazard Evaluation, F. L. Mayer and J. L. Hamelink (*Eds.*) ASTM STP 634, American Society for Testing and Materials.

Harada, Y., Minamata Disease. Shuhan Co., Kumamoto Japan, p73, 1968

Irukayama, K., Fujiki, M., Kai, F. and Kondo, T., Studies on the origin of the causative agent of Minamata Disease.- I. Organic mercury compound in the fish and shellfish from Minamata Bay. Kumamoto Med. J., 14(4):157-169, 1961

Irukayama, K., Fujiki, M., Kai, F. and Kondo, T., Studies on the origin of the causative agent of Minamata Disease.- II. Comparison of the mercury compound in the fish and shellfish from Minamata Bay with mercury compounds experimentally accumulated in the control shellfish. Kumamoto Med. J., 15(1):1-12, 1962-a

Irukayama, K., Fujiki, M., Kai, F. and Kondo, T., Studies on the origin of the causative agent of Minamata Disease.- III. Industrial wastes containing mercury compounds from Minamata Factory . Kumamoto Med. J., 15(2):57-68, 1962-b

Ishizaki, A. and Fukushima, M., Studies on Itai-itai disease. Japan J. Hyg.23, 271-185, 1968

Kasuya, M. Teranishi, H. , Aoshima, K., Katoh, T., Horiguchi, H., Morikawa, Y. Nishijo, M. and Iwata, K., Water pollution by cadmium and the onset of Itai-itai disease. In Matsui, S., Edit: Hazard Assessment and Control of Environmental Contaminants in Water. pp182-189, Proceedings of IAWPRC Symposium, T.I.C.Ltd. ISSN-0917-6888, Osaka, 1991.

Kudo, A. and Hart, J. S., Uptake of inorganic mercury by bed sediments. J. Environ. Qual., 3(3):273-278,1974

Kudo, A., and Gloyna, E. F., Transport of 137 Cs-II. Interaction with bed sediments. Water research., 5:71-79,1971

Kudo, A. and Miyahara, S., Predicted restoration of the surrounding marine environment after an artificial mercury decontamination at Minamata Bay, Japan--Economical value for natural and artificial processes. In Matsui, S., Edit: Hazard Assessment and Control of environmental Contaminants in Water. pp174-181, Proceedings of IAWPRC Symposium, T.I.C.Ltd. ISSN-0917-6888, Osaka, 1991.

Kurachi, M., ***et al.***, A study on the treatment of hazardous waste water from Kamioka Mine. The report of the Study Group on Metal Pollution of Kyoto University, 1980

Odum, E. P., Fundamentals of Ecology, W. B. Saunders Company, Philadelphia, 1959

Southworth, G. R., Parkhurst, B. R., Hebes, S. E. and Tsai, S.C., The risk of chemicals to aquatic environment. In Conway, R. Edit.: Environmental Risk Analysis for Chemicals, pp91-92. Van Nostrand Reinhold, New York, 1982

Tokuomi, H., Minamata Disease. Shuhan Co., Kumamoto Japan, p37,1968

Thompson, S.E., Burton, C.A., Quinn, D.J. and Ng, Y.C., Concentration factors of chemical elements in edible aquatic organisms. UCRL - 50564, Rev.1, Lawerence Livermore Laboratory, 1972.

USEPA Technical Support Document for Water Quality-based Toxic Control, 1991

Walker, C.H. Prog. Drug Metab. 5:113-65,1980

Yanagisawa, M., Shinmura, Y., Yamada, N., Segawa, A., and Kida, K.. Heavy metal pollution and methods of restoration of polluted soil in the Jinzu River basin. Bull. Toyama Agricultural Experimental Stat, 15:1-110, 1984

CHAPTER 4

MODELLING OF LAKE ECOTOXICOLOGY

S.E. Jørgensen

4.1 INTRODUCTION

When toxic substances originating from pesticides, deposition of air pollutants and industrial uses are discharged into lakes they threaten the entire ecology of the lake ecosystem.

Toxic substances interact with many processes in the lake. It is, therefore, necessary to use modelling as an overviewing and synthesizing tool in order to relate quantitatively the discharge of a toxic substance to a lake or reservoir and the damage in the lake at the organism or eco-system level. The general use of modelling in lake management was discussed in Guidelines on Lake Management, Volume 1, Chapter 6, "Use of Models". This chapter will therefore focus entirely on the modelling of toxic substances in lakes and reservoirs.

Quantification, including the use of quantitative relations between the discharge of toxic substances and their effects, is becoming of greater significance in environmental management. This has prompted the development of toxic substance models as an essential part of ecological modelling. Many achievements in the abatement of pollution by toxic substances have been made. For instance, the application of DDT has been banned in many industrialized countries and lead-free gasoline is now in use in the USA, Western Europe and Japan. However unfortunately many environmental problems related to toxic substances remain, as can be seen in Chapters 5 and 6.

The development of toxic substance modelling began in the mid- seventies. The experience gained during the last 15 years can be summarized as follows:

1. Our knowledge about ecotoxicological processes is generally less than our knowledge about ecological processes.
2. *If we want to model all possible combinations of toxic substances, their processes and their interactions with living organisms then the number of parameters we need to know is very large.* If we consider that there are about 50,000 toxic substances produced in such quantities that they may threaten the environment, that the number of parameters for each toxic substance is at least ten, that each of these parameters vary by species, and that to get a representative picture of all species we should at least examine the interactions of, let us say 1000 species, **then we are required to consider 500 million parameters (50,000 $*$ 10 $*$ 1,000 parameters).**
3. Fortunately, *in most cases we do not need to model ecotoxicological problems very accurately,* because we aim for the application of **a wider margin of error.**

Consequently ecotoxicological models differ from general ecological models as follows:

1. they are often **more simple**,
2. requiring **more parameters**,
3. **use less accurate methods for parameter estimation**, and
4. possibly include **an effect component**.

Ecotoxicological models can be divided into five classes. The classification presented here is based on differences in the modelling structure. The decision as to which model class to use is based on the ecotoxicological problems that the model is going to solve. This classification is different from the classifications presented in Chapter 6 of Guidelines on Lake Management, Volume 1 because it is based on the actual problem that is modelled rather than on the mathematics or philosophy behind the model. The definitions of the model classes are given below and the most appropriate use of each of the model type is indicated.

1. Food chain or food web dynamic models.
This class of models considers the flow of toxic substances through the food chain or food web. Such models are relatively complex and contain many state variables. The models furthermore contain many parameters. This class of models should be used where the problems are of crucial importance and the underlying data base is comprehensive.

2. Static models of the mass flows of toxic substances.
If seasonal changes are of minor importance, the application of a static model of mass flows should be considered. Simulations will indicate how the static model changes at different levels of emissions.

3. Dynamic models of toxic substances at a trophic level.
If the "ecotoxicological alarm clock" is a single trophic level, as in the mercury contamination of fish, it is often sufficient to develop a model for that trophic level.

4. Ecotoxicological models in population dynamics.
These are biodemographic models and are mainly used to indicate the effect of a toxic substance on the population level.

5. Ecotoxicological models with effect components.
This type of model includes a translation of a concentration into an effect, but is otherwise not different from the other types. Inclusion of the effect component requires knowledge to the lethal and/or sub-lethal level.

A few points need to be emphasized here before entering a discussion of the modelling procedure. The modeller should:

1. Obtain the best possible information about the processes of the toxic substance under consideration. Section 4.2 will review the various ecotoxicological processes and how

they are described in the modelling context.

2. Attempt to get parameters of the toxic substance processes in the environment and the literature. This is discussed in Section 4.3.
3. Estimate all parameters using the methods discussed in Section 4.3.
4. Compare the results from 2. and 3. and attempt to explain any discrepancies present.
5. Use sensitivity analysis to estimate which processes and state variables should be included in the model. It is better to develop an overly-simple rather than an overly-complex model.

4.2 PROCESS MODELLING

Ecotoxicological processes differ from other ecological processes. A review of the relevant processes and their quantitative description is therefore needed. The most crucial ecotoxical processes and the most frequently applied mathematical descriptions of these processes are provided below.

4.2.1 Concentration factor

This factor relates the concentration in water (the medium) with the concentration in organisms, sediment or suspended matter. The concentration in organisms is a result of the uptake by respiration, and the concentration in sediment or in suspended matter is caused by adsorption and sedimentation processes. It is often sufficiently accurate to describe the concentration factor, CF, as a constant independent of the concentration in the medium:

$$CF = CS / CW, \qquad (4.1)$$

where CS is the concentration in the organisms, suspended matter or sediment, while CW is the concentration in water. If the uptake includes indirect uptake through the foodchain, then the expression "biological accumulation factor" (BAF) is often used. $BAF \geq CF$, but may be described by the same equation.

Table 4.1 gives equations relating the water solubility (S) and partition coefficient (Kow) to CF and BAF. The partition coefficient is the ratio of solubility in octanol and water for the organic compound under consideration. If the partition coefficient is not known, it is possible to estimate it from the water solubility (see Fig. 4.1). The distribution coefficient (Koc) for water/soil is defined under the condition that the soil is 100% organic matter. If the soil has only a fraction foc, which is organic matter, the distribution coefficient becomes: Kocfoc.

Table 4.1 Regression Equations for Estimation of Bioconcentration, Bioaccumulation and Biomagnification Factors (BCF, BAF, BMF)

Indicator	Relationship	Correlation coefficient	Range (indicator)
Kow	log BCF = -0.973 + 0.767 log Kow	0.76	$2.0*10^{-2}$ - $2.0*10^{6}$
Kow	log BCF = 0.7504 + 1.1587 log Kow	0.98	7.0 - $1.6*10^{4}$
Kow	log BCF = 0.7285 + 0.6335 log Kow	0.79	1.6* - $1.4*10^{4}$
Kow	log BCF = 0.124 + 0.542 log Kow	0.95	4.4*100 - $4.2*10^{7}$
Kow	log BCF = -1.495 + 0.935 log Kow	0.87	1.6*100 - $3.7*10^{6}$
Kow	log BCF = -0.70 + 0.85 log Kow	0.95	1.0 - $1.0*10^{7}$
Kow	log BCF = 0.124 + 0.542 log Kow	0.90	1.0*100 - $5.0*10^{7}$
Koc	log BAF = 2.024 + 1.225 log Koc	0.91	0.4 - $4.3*10^{4}$
Koc	log BAF = 1.579 + 1.191 log Koc	0.87	3.2 - $1.2*10^{6}$
S(mg/l)	log BAF = 2.183 - 0.629 log S	0.66	$1.7*10^{-3}$ - $6.5*10^{5}$
S(μg/l)	log BAF = 3.9950 - 0.3891 log S	0.92	1.2 - $3.7*10^{7}$
S(μg/l)	log BAF = 4.4806 - 0.4732 log S	0.97	1.3 - $4.0*10^{7}$
S(mg/l)	log BAF = 2.791 - 0.564 log S	0.72	$1.7*10^{-3}$ - $6.5*10^{5}$
S(μmol/l)	log BAF = 3.41 - 0.508 log S	0.96	$2.0*10^{-2}$ - $5*10^{3}$
S(μmol/l)	log BMF = -0.4732 log S + 4.4806	-	
S(μmol/l)	log BMF = -0.3891 log S + 3.995	-	

4.2.2 Biomagnification

This describes the process whereby pollutants are passed from one trophic level to the next, and exhibit increasing concentrations in organisms related to their trophic status. The magnification (i.e. the increasing concentration through the foodchain) is caused by a higher retention of toxic substances than of general food components in the organisms. The process may be described by the so-called biological or ecological magnification factor, which indicates the magnification from one level in the food chain to the next. Table 4.1 shows some relationships between water solubility and biomagnification factor (BMF).

4.2.3 Adsorption

This may be described as indicated above by simply using a concentration factor. However, at time it may be more accurate to use Freundlich or Langmuir adsorption isotherms.

4.2.4 Solubility

This is a key parameter in ecotoxocological modelling as other parameters are estimated from the water solubility, as demonstrated in Table 4.1. The relationship between the partition coefficient (Kow) and the water solubility (S) is shown in Figure 4.1.

Table 4.1, continued

Animal	Number of Chemicals	References
Fish species	36	Kenaga and Goring, 1978
Mosquito fish	9	Metcalf et al., 1975
Mosquito fish	11	Lu and Metcalf, 1975
Trout	8	Neely et al., 1974
Fish species	26	Kenaga and Goring, 1978
Fathead minnow	59	Veith et al., 1979
Fathead minnow, bluegill, mosquito fish, rainbow trout, green sunfish	59	Lassiter, 1975
Fish species	22	Kenaga and Goring, 1978
Fish species	13	Kenaga and Goring, 1978
Fish species	50	Kenaga and Goring, 1978
Mosquito fish	11	Lu and Metcalf, 1975
Mosquito fish	9	Metcalf et al., 1975
Fish species	36	Kenaga and Goring, 1978
Trout	7	Chiou et al., 1977
Mosquito fish, whole		Metcalf et al., 1975
Mosquito fish, whole		Lu and Metcalf, 1975

4.2.5 Excretion

It can be shown that the excretion of toxic substances by organisms follows a first-order kinetics with good approximations and that the rate coefficient is dependent on the chemical compound and the size of the organism considered (see Jørgensen, 1988 and 1990). This process is in most cases insignificant for the entire mass balance for the components under consideration, but it may be important to include the excretion process for a model of a toxic substance at the organism level.

4.2.6 Biodegradation rate

The general mathematical expression used to relate the rate of microbiological growth was first suggested by Monod (1949):

$$dX/dt = \mu max\ X\ S / (Km + S), \tag{4.2}$$

where μmax is the maximum specific growth rate; Km is the so-called half-saturation constant, which is the concentration of S corresponding to half of the maximum growth rate, S is the concentration of the substrate, and X is the concentration of microorganisms.

In most cases of ecotoxicological interest, the substrate concentration is low, and (4.2) may be changed to a second-order or a pseudo first-order reaction scheme. The latter is valid when the concentration of microorganisms is constant, for instance under constant environmental conditions.

However, it is rather difficult to estimate the reaction rate of biodegradation in ecotoxicology, because a large number of factors influence the reaction considerably and thereby also the concentration of microorganisms. The most important of these factors are:

Temperature. This factor may be taken into consideration by use of the following equations:

$$K_t = K_{20}\, \theta^{\, t - 20} \tag{4.3}$$

$$K_t = K_{20}\, (1.06 - 1.09)^{t - 20} \tag{4.4}$$

where K_{20} is the biodegration coefficient at 20°C and θ is temperature constant, with values depending on environmental conditions. In some cases such as waste stabilization ponds θ can be in the range of 1.06 to 1.09. It can be expressed in g, or moles per unit of time, or in g or moles per unit of time and per kg biomass. The latter units are used when the influence of the microorganism concentration (X) is considered.

Adaptation. A natural microbial population's previous exposure to a particular chemical compound often has a great influence on the degradation rate. Detailed examination is required to model the adaptation period and in most cases it is therefore necessary to assume that the adaptation is either complete or has not yet been initiated.

Sorption. This process was discussed above. Its influence on biodegradation is simply considered by the inclusion of sorption isotherms in the model.

Redox potential. This environmental property determines which terminal electron acceptor is used and thereby the composition of microorganisms. Significantly increased (see, e.g., Larson *et al.*, 1981) as well as decreased (see, e.g., Pritchard *et al.*, 1979) rates of biodegradation have been observed in anaerobic environments.

Ionic strength. The degradation rate will generally decrease as the ionic strength increases.

Nutrients. Microbial growth is affected by major nutrients as well as by essential micronutrients (including trace metals). The composition of microorganisms indicates that the biomass contains approximately 0.5 - 1.0% phosphorus and 5 - 9% nitrogen. The effect of nitrogen and phosphorus limitation on the biodegradation of hydrocarbons in seawater is significant for the solution of this ecotoxicological problem (see Atlas, 1981).

Sediment composition. Rates of biodegradation vary considerably for various types of soil due to differences in the availability of organic nutrients for microorganisms. Some semi-qualitative rules for the relationship between molecular structure and rate of biodegradation may be set up:

1. *Aromatic compounds* are generally less biodegradable than aliphatic compounds.
2. *The higher the molecular weight,* the less biodegradable is the compound.
3. The *more substitutes* the molecule contains, the less biodegradable the compound is.

4. *Double bonds* will generally increase the biodegradability.
5. *-O- and -N=* will generally decrease the biodegradability.

A quantitative relationship between biodegradation kinetics and structure exists, but it is weak, particularly because the environmental factors mentioned above play a major role.

It has often been shown in various literature that biodegration (or the biological half-life) occurs after 7 days incubation (BD7). These values may be found in Jørgensen *et al.* (1991) and Jørgensen (1991).

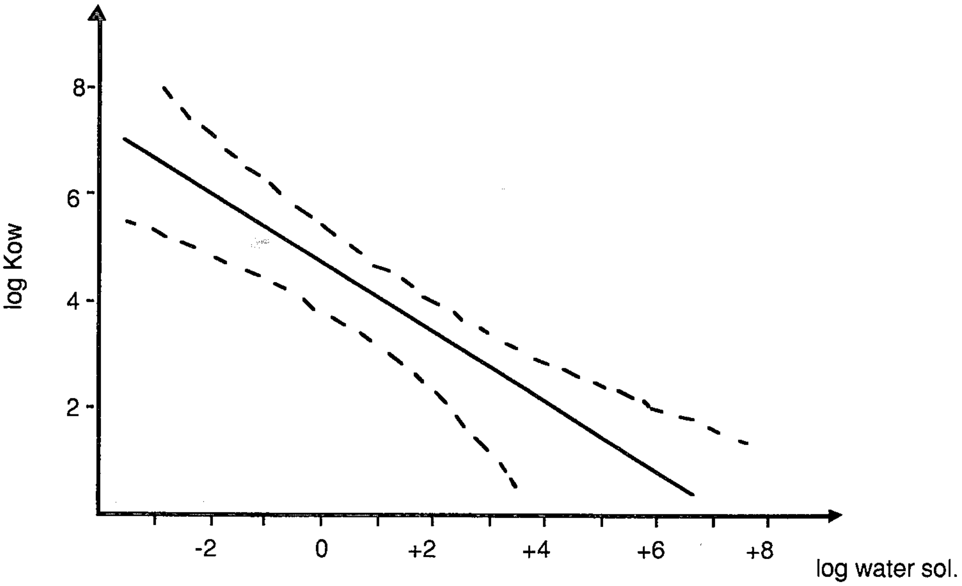


Fig. 4.1. Relationship between the logarithm of the water solubility, S, at room temperature and expressed as mmol/l and logarithm of the partition coefficient, Kow, at room temperature. Reproduced from Chiou *et al.* (1977) and Banerjee *et al.* (1980).

4.2.7 Distribution air-water

$$\frac{C^*}{To^*} \equiv F_L = \frac{H\,18}{1000R\,T} \qquad \text{(approximation)} \qquad (4.5)$$

or, by 1 atm and 20°C

$$F_L = 7.49\ 10^{-4}\ H \qquad (4.6)$$

where F_L is air-water distribution ratio, and H is Henry's constant (atm.),

C* and To* are equilibrium concentrations (weight/volume) in air and water respectively.

4.2.8 RATE OF EVAPORATION

$$Ev = -DA \frac{dTo}{dx} = b\,KL\;\;A\;\;(To - To^*)\quad , \tag{4.7}$$

where Ev is evaporation rate, and D is the molecular diffusion coefficient ($L^2\ T^{-1}$), A is the area, and b is a coefficient which adjusts the aeration coefficient (LT^{-1}) to compounds other than oxygen (b = 1.0 for oxygen). b can be found in Jørgensen (1991) for other compounds. Several empirical equations for calculating KL can be found in Jørgensen and Gromiec (1989) or Jørgensen and Johnsen (1989).

Notice that

$$b = \frac{KL\ compound}{KL\ oxygen} = \frac{D\ compound}{D\ oxygen} \tag{4.8}$$

For lakes and streams, it can be shown that

$$To(t) = To(0)\,e^{-bKLat} \tag{4.9}$$

where

$$a = \frac{A}{V} = \frac{area}{volume} \tag{4.10}$$

4.2.9 Distribution water-solid (sediment)

A distribution coefficient may be used at low concentrations (see also Langmuir's and Freundlich's adsorption isotherms):

$$Fs \equiv \frac{C^*}{To^*} \tag{4.11}$$

where Fs water-solid distribution ratio and C* and To* are the concentrations in the solid and water phases at equilibrium. Since the unit of C* is MM^{-1} (for instance mg/g dry matter) and To* has the unit of ML^{-3}(mg/l), Fs gets the unit L^3M^{-1} (l/g or l/kg).

Fs may be found from

$$Fs = Foc * foc \tag{4.12}$$

where Foc is the distribution coefficient for organic matter (Koc is also used in the same context) and foc is the fraction of organic carbon in the solid under consideration.

The following relationship between Foc and Kow exists (Brown and Flagg, 1981):

$$\log Foc = -0.006 + 0.937 \log Kow \tag{4.13}$$

Matter-Muller *et al.* (1980) found the following relationship for activated sludge:

$$\log Fs = 0.39 + 0.67 \log Kow \text{ (l/kg for Fs)} \quad (4.14)$$

Foc- and Fs-values for selected chemical compounds can be found in the literature.

4.2.10 Complex formations

As for other chemical processes, the mass equation is valid for these reactions. For the process:

$$Men^{+} + Lm^{-} \rightarrow MeL(n\text{-}m)^{+} \quad (4.15)$$

where Me denotes a metal and L a ligand. In this case the mass equation assumes the following form:

$$\frac{[MeL(n\text{-}m)^{+}]}{[Men^{+}]\,[Lm^{-}]} \quad (4.16)$$

K is the stability constant if the process is the formation of a complex.

The coordination number of a metal is the number of bonds formed from the metal ion to the donor atoms of the ligands. Even coordination numbers (2, 4, 6 and 8) are much more common than uneven ones, **coordination numbers 4 and 6 being most frequently encountered.**

The formation of *coordination complexes* plays a major role in modelling the distribution as well as the effect of metal ions in aquatic ecosystems due to the following influences:

Increase of metal solubility.

$$MeY(S) = L = MeL + Y \quad (4.17)$$

where Me represents a metal which is bound in the sediment in the compound MeY, and L denotes a ligand;

Alteration of the distribution between oxidized and reduced forms of metals. The equilibrium constant for the process

$$Men^{+} + me^{-} \rightarrow Me(n\text{-}m)^{+}$$

differs from the one for

$$MeLn^{+} + me^{-} \rightarrow MeL(n\text{-}m)^{+}$$

if the complexes MeLn+ and MeL(n-m)+ have different stability constants, which is often the case;

Alleviation of toxicity due to alteration of the availability to aquatic life;

Change in adsorption and ion exchange of sediment and suspended matter, and

Change in stability of the metal-containing colloids.

The presence of ligands in water will generally increase the transfer of metals from sediment, soil and suspended matter and thereby increase the solubility. However, as complexes show lower toxicity than the metal ions, the harm to the aquatic life in most cases does not increase corresponding to the increased solubility.

The application of *coordination chemistry to environmental problems* is very complex, as a great number of ligands are present in aquatic ecosystems with all the ligands competing simultaneously in the formation of complexes with the metal ions.

4.2.11 Photolysis

Some chemical species in natural waters absorb light energy directly, and undergo direct photochemical reactions. Examples of this type are the photolysis of nitrate, nitrite and methyl iodide in seawater (Zafiriou and True, 1979a, 1979b; Zafiriou and McFarland, 1981; Zika *et al.*, 1984). If the products are still reactive, such as singlet oxygen and hydrogen peroxide, further reactions may occur (Van Baalen and Marler, 1966; Joussot-Dubien and Kadiri, 1970; Zepp *et al.*, 1977; Baxter and Carey, 1982; Haag et al, 1984a, 1984b). Only light that is absorbed by a molecule can produce chemical changes. This fundamental law of photochemistry has been recognized since the early nineteenth century by Grotthus and Draper. The absorption of light by a molecule is governed by the Lambert-Beer law. Thus the initiation of photochemical reactions will depend on the spectral characteristics and the intensity of the incident light and the ability of a given chemical species to absorb light at various wavelengths.

The molecule which has absorbed light becomes 'energy-rich' or 'excited'. **The Stark-Enstein law** states that if a species absorbs radiation, then one particle is excited for *each quantum* of radiation absorbed. The energy is of course limited by the energy of the photon absorbed. This energy is given by:

$$E = h\,v \tag{4.18}$$

where E is the energy of the photon, h is the Planck's constant and v is the frequency of the photon. Thus, depending on the nature of the incident light and the property of the chromophore, different excited states of the chromophore may be formed. Although it is not exclusively true, in general light absorption which results in photochemical reactions causes electronic excitation of the chromophore. Excitation of the vibrations and rotations of the absorbing species in its ground electronic state is less likely to induce chemical changes.

The effectiveness of photochemical reactions in the consumption or production of a given chemical species is given by **the overall quantum yield**, b, of that process. The overall quantum yield is the number of molecules of a given reactant consumed for each photon absorbed. It may be further subdivided into that which is caused by primary reactions, or primary quantum yield, and that which is caused by secondary reactions.

Since more than one primary reaction may be involved in a photochemical reaction, the primary quantum yield may be defined with respect to a specific primary reaction. Moreover, the sum of the quantum yields of all primary reactions, including de-activation, must be unity. The overall quantum yield, which is the quantity most often determined, on the other hand, does not distinguish between the effects of primary and secondary reactions, and it may exceed unity.

Modelling photochemical reactions in natural waters is still in its infancy. No proven general model applicable to every kind of natural water is presently available for the estimation of the rates of consumption or production of chemical species through light-induced reaction pathways. A great deal of information on the construction of precise and realistic models is still not available. For example, the chemical composition of natural waters and their temporal and spatial variabilities are still inadequately known. Thus, the reactants that may participate directly and indirectly in photochemical reactions in a competitive, synergistic or catalytic manner cannot yet be fully identified. The rate at which a particular photochemical reaction may proceed in this poorly defined medium, and to which extent it will proceed *cannot* be quantified *without* extensive empirical data. Moreover, as stated previously, even in a well-defined medium, the detailed reaction pathways of photochemical reactions can still rarely be identified definitely.

Despite these limitations, several investigators have attempted to construct models for estimating the rates of direct photolysis, a specific type of photochemical reaction, in natural waters under restricted conditions (Zepp and Cline, 1977; Mancini, 1978; Zepp and Baughman, 1978; Zepp, 1978, 1982a, 1982b).

For an incident beam of light with a certain spectral characteristic, if the quantum yield is not strongly wavelength-dependent (Turro, 1965), the complete rate law for direct photolysis will be:

$$-(d[C_A] / dt) = ka[C_A] \tag{4.19}$$

where ka is the sum of the ka x l values of all the wavelengths represented by the photons in the incident light. For further details of this important process refer to Wong (1989).

4.2.12 Acid-base reactions

These reactions are of great environmental interest, because almost all processes in the environment are dependent on pH. A few illustrative examples are included in the following list:

1. Ammonia is toxic to fish and the ratio of ammonium to ammonia is known to be dependent on pH.
2. Carbon dioxide is toxic to fish and the ratio of bicarbonate to carbon dioxide is dependent on pH.
3. The fertility of fish and zooplankton eggs is highly dependent on pH.
4. All biological processes have a pH-optimum, which is usually in range 6-8. This implies that algal growth, microbiological decomposition, nitrification and denitrification ar all influenced by pH.
5. The release of heavy metal ions from soil and sediment increases very rapidly with decreasing pH. Heavy metal hydroxides have a very small solubility product, which implies that most heavy metal ions are precipitated at Ph 7.5 or above.

The concern for acid rain illustrates the problems related to low pH, but overly-high pH is also of environmental concern due to points 1 and 4 mentioned above. It is therefore understandable that assessments, computations or predictions of pH and the buffer capacities are important elements in many models in environmental chemistry.

The buffer capacity β is defined as:

$$\beta = dC / dpH \tag{4.20}$$

pH and β are often found by the use of an additional submodel. The application of the double logarithmic representation of proteolytic species is recommended here, because this method is easy to use even for rather complex acid-base systems. This approach is presented below.

The concentrations of proteolytic species are characterized by the total alkalinity Al, and pH. The total alkalinity is determined by adding an excess of a standard acid (eg. 0.1 M), boiling off the carbon dioxide formed and titrating back to a pH of 6. During this process all the carbonates and hydrogen carbonates are converted to carbon dioxide and expelled and all the borate is converted to boric acid. The amount of acid used (i.e. the acid added minus the base used for back titration) then corresponds to the alkalinity, Al, and the following equation is valid:

$$Al = C_{H2BO3-} + 2C_{C032^-} + C_{BO3^-} + (C_{OH-}\, C_{H+}) \tag{4.21}$$

where C is the concentration in moles per litre for the indicated species. In other words, the alkalinity is the concentration of hydrogen ions that can be taken up by proteolytic species present in the sample examined. Obviously, the higher the alkalinity, the better the solution is able to maintain a given pH value if acid is added. The buffering capacity and the alkalinity are proportional (see, e.g., Stumm and Morgan, 1970).

Each of the proteolytic species in an aquatic system has an equilibrium constant. If we consider the acid HA and the dissociation process:

$$HA \rightarrow H^+ + A^- \tag{4.22}$$

we have

$$Ka \frac{[H:]\,[A-]}{[HA]} \qquad (4.23)$$

where Ka is the equilibrium constant.

It is possible, when the composition of the aquatic system is known, to calculate both the alkalinity and the buffering capacity, using the expression for the equilibrium constants. However these expressions are more conveniently used in logarithmic form. If we consider the expression for Ka for a weak acid, the general expression (4.22) may be used in a logarithmic form:

$$pH = pKa + \log \frac{[A-]}{[HA]} = pKa + \log[A-] - \log\,[HA] \qquad (4.24)$$

where both sides of the equation are multiplied by -1, and the symbol p is used for "-log" and pH for "-log H^+". It is often convenient to plot concentrations of HA and A- versus pH in a logarithmic diagram (see, e.g., Jørgensen, 1990).

4.2.13 Other chemical processes

In addition to the chemical processes mentioned above, hydrolysis (reaction with water) and redox processes may also play a role in the speciation and general presence of toxic substances in lakes. Many metal hydroxides may be dissolved by hydrolysis, and the release of metal ions from the lake sediment is very dependent on redox potential at the interface between water and sediment. Organic compounds may also react by hydrolysis. For instance, many compounds will react with water and thereby introduce a hydroxide group. Also redox reactions cause many organic toxic compounds to be oxidized by oxygen and carboxyl groups may be formed.

For all these reactions a chemical pathway should be found. Application of simple first-order reaction kinetics will often be sufficient for a description of the process in an ecotoxicological model.

4.3 PARAMETER ESTIMATION

As mentioned in the introduction to this chapter, the number of parameters needed for modelling in ecotoxicology is very high and only a small proportion can be found in the literature. It is therefore necessary to use estimation methods for those parameters not found in the literature.

The physical properties of interest in ecotoxicology are vapour pressure, water solubility, partition coefficient, mass transfer coefficient for transfer between air and water, adsorption isotherms and diffusion coefficients. It is possible to estimate all these properties on the basis of knowledge of the chemical structure of the organic compounds. Some of the estimation methods are based on an estimation of the boiling point and the critical properties, which are then used to estimate the above-mentioned physical properties (see, i.e., Jørgensen, 1990). Experience with the use of such estimation methods shows that it is generally possible to give better estimates if the boiling point is known. The simultaneous use of two or more estimation methods will always give a better over-all estimation -- an average value is used -- than if only one method is applied. It is possible to estimate chemical properties as well (i.e. rate of hydrolysis, rate of oxidation and/or reduction, and acid dissociation coefficients).

Obviously, biological properties are very important in ecotoxicological modelling, and since these properties generally are even less known than the physical and chemical properties, the estimation methods are more important. Fig. 4.2 shows how it is possible to estimate BCF, BAF and BMF by use of solubility data (S) and partition coefficients (Kow); these relations are also discussed in Section 4.2. Furthermore, from the structure it is possible to estimate biodegradation rate coefficients and toxicity. Some of the methods work via molecular weight (M) and estimations of melting point (Tm) and boiling point (Tb) (see Fig. 4.2).

The estimation methods used in practical ecotoxicological modelling have been widely tested on compounds with more or less known properties, and it has been found that the estimation methods have a standard deviation of 10-50% for most parameters. This is an acceptable accuracy, considering that wide margins of error are recommended and applied in ecotoxicological modelling. Although the number of relevant parameters that can be found in the literature is limited, it is of course an advantage to review the literature to find the parameters that actually have been determined. It is furthermore an advantage to compare the parameters that have been estimated by various methods to get an impression of the accuracy of these methods for the compounds under consideration. The following references may be used as primary sources: Jørgensen *et al.* (1991), Jørgensen (1991, 1990), Samiullah (1990) and Verschueren (1977).

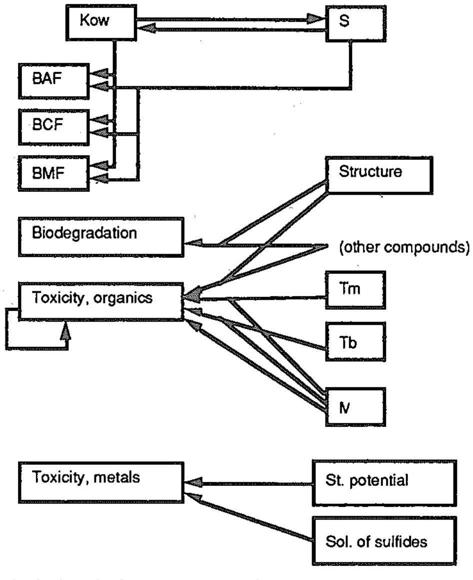


Fig. 4.2 Relationships between physical-chemical parameters and molecular structure on the one side, and biological parameters on the other.

4.4 OVERVIEW OF TOTAL MODELS

Table 4.2 reviews some of the models that are in use or could be used (they are developed for other aquatic systems, but could in principle be used directly for lake studies) in lake management. The models that are indicated with a +) are those developed directly for a lake study.

Table 4.2 Examples of Toxic Substance Models

Toxic substance	Model characteristics	Reference
Cadmium +)	Food chain similar to a eutrophication model	Thomann *et al.*, 1974
Mercury +)	6 state variables: water, sediment, suspended matter, invertebrates, plants and fish	Miller, 1979
Vinyl chloride	Chemical processes in water	Gillett *et al.*, 1974
Methyl parathion	Chemical processes in water and benzothiophene, microbial degradation, adsorption, 2-4 trophic levels	Lassiter, 1978
Methyl mercury +)	A single trophic level: food intake, excretion, metabolism growth	Fagerstrom and Aasell, 1973
Heavy metals	Concentration factor, excretion, bioaccumulation	Aoyama *et al.*, 1978
Pesticides in fish	Ingestion, concentration factor, adsorption in body, DDT & methoxychlor defecation, excretion, chemical decomposition, natural mortality	Leung, 1978
Zinc in algae	Concentration factor, secretion, hydrodynamical distribution	Seip, 1978
Copper in sea	Complex formation, adsorption, sub-lethal effect of ionic copper	Orlob *et al.*, 1980
Lead +)	Hydrodynamics, parecipitation, toxic effects of free ionic lead on algae, invertebrates and fish	Lam and Simons, 1976
Radionucleides	Hydrodynamics, decay, uptake and Gromiec and release by various aquatic surfaces	Gromiec and Gloyna, 1973
Cadmium, PCB	Hydraulic overflow rate (settling), sediment interactions, steady state food chain submodel	Thomann, 1984

Table 4.2 continued

Toxic substance	Model characteristics	Reference
Hydrophobic organic compounds +)	Gas exchange, sorption/desorption, hydrolysis, photolysis, hydrodynamics	Schwarzenbach and Imboden, 1984
Mirex +)	Water-sediment exchange processes, adsorption, volatilization, bioaccumulation	Halton, 1984
Toxins (aromatic hydrocarbons,Cd)	Hydrodynamics, deposition, resuspension, volatilization, photooxidation, decomposition, adsorption, complex formation, (humic acid)	Harris *et al.*, 1984
Heavy metals	Hydraulic submodel, adsorption	Nyholm, Nielsen & Pedersen, 1984
Oil slicks	Transport and spreading, influence of surface tension, gravity and weathering processes	Nihoul, 1984
Acid rain +)	C, N and S cycles and their influence on acidity	Arp, 1983
Chromium	Distribution, sedimentation and benthic fauna	JØrgensen, 1990
Copper +)	Sediment-water interactions, complex formations	JØrgensen, 1990
Mercury	Distribution, sediment-water interactions, bioaccumulation	JØrgensen, 1990
Chloro- benzenes +)	Distribution, sediment-water interactions, adsorption and biomagnification	JØrgensen, 1990

It is not possible here to give details of all of the ecotoxicological lake models, but three examples serve to illustrate the factor involved. Fig. 4.3 gives the conceptual diagram for a copper model (Jørgensen, 1990), Fig. 4.4 for a mercury model (Jørgensen *et al.*, 1990), and Fig. 4.5 for a model of chlorobenzenes in a large lake system (Halfon and Oliver, 1990).

These three cases illustrate, like most of the other lake ecotoxicological case studies, that different processes are important for different case studies (i.e. a good knowledge of the problem (the toxic compound and the lake system) is the best basis for the development of a good workable management model). Experience shows that if the right complexity and the right processes are selected for the model then applicable models can be developed and used in environmental management.

The copper model (Fig. 4.3) considers the details of the copper speciation, because it is the key factor determining the water-sediment exchange of copper. The copper ion concentration is the alarm clock, because copper ions are toxic to the lake fauna. For mercury (Fig. 4.4) the methylation processes and the biomagnifications are the most important processes and the alarm clock is here the mercury concentration in fish used for human consumption. For chlorobenzenes (Fig. 4.5) the biomagnification, the adsorption processes and the water-sediment exchange processes are the most important processes.

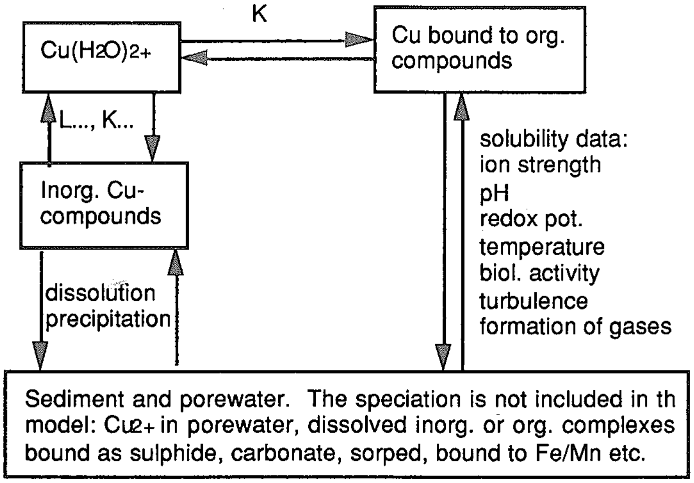


Fig. 4.3 Conceptual diagram for copper in a lake.

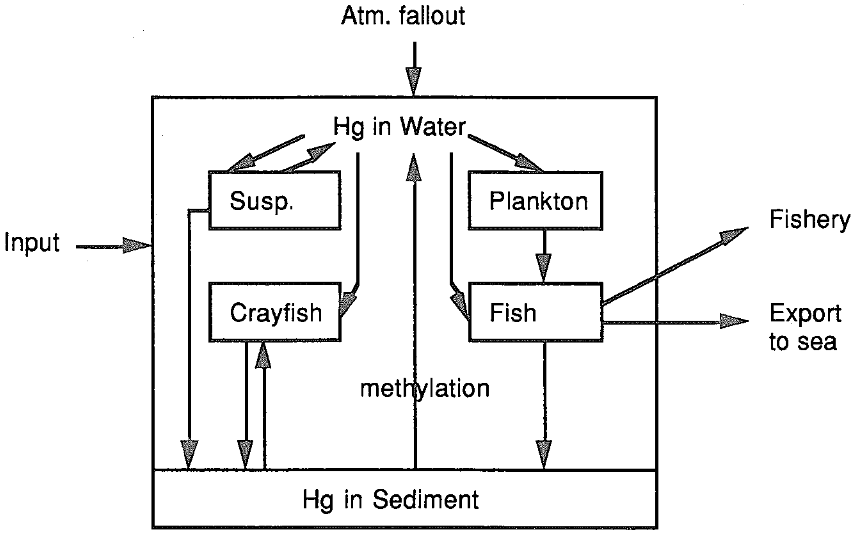


Fig. 4.4 Conceptual diagram for mercury in an aquatic ecosystem.

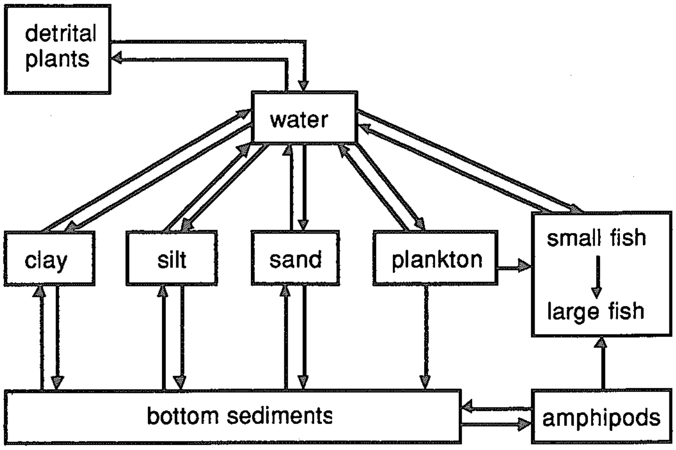


Fig. 4.5 Structure and state variables of the model TOXFATE. The arrows indicate the possible direction of flow of toxic contaminants between compartments. The state variables are the concentrations of the contaminants in each part of the ecosystem.

4.5 CONCLUSIONS

This review of ecotoxicological lake models and the presentation of our present knowledge about ecotoxicological processes in lakes has demonstrated that it is feasible today to develop workable models that are capable of describing ecotoxicological problems of lakes, and that furthermore can be used in a management context. We have reasonable experience today in the development of ecotoxicological models, and we have been able to model a reasonably wide spectrum of toxic compounds in the environment. However, much more experience is desirable to gain more knowledge about the development of such models and to be able to reduce the uncertainty of today's models.

This chapter has presented estimation methods for parameters of ecotoxicological models. These methods are in a very initial stage of development and, as pointed out, their certainty should be improved in the coming years; this will allow models to make predictions with higher accuracy than today. Our process descriptions may also be improved, but this is probably the element of our models which is the furthest developed today and where the least progress would be expected.

Our experience with ecotoxicological models is only about 10-15 years old. Seen in this light, we are making perfectly acceptable models. However time must be devoted to improving the models further, particularly with respect to their certainty and to their application in management and research. What we have already achieved so far looks promising for the results of modelling lake ecotoxicology in the coming decade.

4.6 REFERENCES

Aoyama, I. *et al.* (1978). Simulation analysis of the concentration process of trace heavy metals by aquatic organisms from the viewpoint of nutrition ecology. Water Research 12, 837-842.

Arp, P.A., (1983). Modelling the effects of acid precipitation on soil leachates: A simple approach. Ecological Modelling 19,105-117.

Atlas, R.M. and Bartha, R. (1973). Stimulated biodegradation of oil slicks using oleophilic fertilizers. Environ. Sci. Technol 7, 538.

Banerjee, S. *et al.* (1980). Water solubility and octano/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlations. Environ.Sci. Technol. 14,1227.

Baxter, R M, and Carey, J.H. (1988). Reactions of singlet oxygen in humic waters. Freshwater Biol. 12,285-292.

Chiou, C.T. *et al.* (1977). Partition coefficient and bioaccumulation of selected organic chemicals. Environ. Sci. Technol. 11,475-478.

Fagerstroem, T. and Aasell, B (1973). Methyl mercury accumulation in an aquatic food chain. A model and implications for research planning. Ambio 2, 164-171.

Gillett, J.W. *et al.* (1974). A conceptual model for the movement of pesticides through the environment. National Environmental Research Center, US Environmental Protection Agency, Corvallis, OR Report EPA 660/3-74-024, p.79.

Gromiec, M.J. and Gloyna, E.F. (1973). Radioactive transport in water. Final Report No. 22 to US Atomic Energy Commission, Contract AT(11-1)-490.

Haag, W.R. *et al.* (1984a). Singlet oxygen in surface waters. Part I: Furfuryl alcohol as a trapping agent. Chemosphere, 13, 631-640.

Haag, W.R. *et al.* (1984b). Singlet oxygen in surface waters. Part II: quantum yields of its production by some natural humic materials as a function of wavelength. Chemosphere 13, 641-650.

Halfon, E. (1984). Error analysis and simulation of mirex behaviour in Lake Ontario. Ecol. Modelling 22, 213-253.

Halfon, E. and Oliver, B.G. (1990). Simulation and data analysis of four chlorobenzenes in a large lake system (Lake Ontario) with toxfate, a contaminant fate model. In Modelling In Ecotoxicology. Edited by S.E. Jørgensen). Developments in Environmental Modelling 16 , 197-214.

Harris, J.R.W. *et al.* ( ). A Preliminary model of the dispersal and biological effects of toxins in the Tamar estuary, England. Ecol. Modelling 22, 253-285.

Joussot-Dubien, J. and Kadiri, A. (1970). Photosensitized oxidation of ammonia by singlet oxygen in aqueous solution and in seawater. Nature 227, 700-701.

Jørgensen, S.E. (1989). Modelling in Ecotoxicology. Elsevier. Amsterdam, Oxford, New York, Tokyo.

Jørgensen, S.E. and Gromiec, M.J. (*Eds.*) (1989). Mathematical Submodels in Water Quality Systems. Elsevier. Amsterdam, Oxford, New York, Tokyo.

Jørgensen, S.E. and Johnson, I. (1989). Principles of Environmental Science and Technology. Elsevier. Amsterdam, Oxford, New York, Tokyo.

Jørgensen, S.E. (*Ed.*) *et al.* (1990). A mercury Model for Mex Bay, Alexandria. In Modelling in Ecotoxicology. Developments in Environmental Modelling 16, 135-148.

Jørgensen, S.E. *et al.* (1991). Handbook of Ecological Parameters and Ecotoxicology. Elsevier. Amsterdam, Oxford, New York, Tokyo.

Jørgensen, S.E. (1991). Modelling in Environmental Chemistry. Elsevier. Amsterdam, Oxford, New York, Tokyo.

Kenaga, E.E. and Goring, C.A.I. (1978). Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota. In Aquatic Toxicology. Edited by J.G. Eaton *et al.* Special Technical Publications, No. 707, 78-13. Amsterdam Society for Testing and Materials, Philadelphia.

Lam, D C.L. and Simons, T.J. (1976). Numerical computations of advective and diffusive transport of chloride in Lake Erie. J. Fish Res. Canada 33, 537-549.

Larson, F.J. and Perry, R.L. (1981). Use of the electrolytic respirometer to measure biodegredation in natural water. Water Res. 15, 697.

Lassiter, R.R. (1978). Principles and constraints for predicting exposure to environmental pollutants. U..S. Environmental Protection Agency, Corvallis, OR Report EPA, 118-127519.

Lassiter, R.R. (1975). Modelling dynamics of biological and chemical components of aquatic ecosystems. U.S. Environmental Protection Agency, Washington DC. EPA-660/3-75-012.

Leung, D.K. (1978), Modelling the bioaccumulation of pesticides in fish. Center for Ecological Modelling Polytechnic Institute, Troy, NY Report 5.

Lu,P.-Y. and Metcalf, R.L. (1975). Environmental fate and biogradability of benzene derivatives as studied in a model aquatic ecosystem. Environmental and Health Perspectives 10, 269-284.

Mancini, J.L. (1978). Analysis framework of photodecomposition in waters. Environ. Sci. Technol. 12, 1274-1276.

Mater-Müller C. *et al.* (1980). Non-biological elimination mechanisms in biological sewage treatment plant. Prog. Wat. Techn. 12, 299-314.

Metcalf, R.L. *et al.* (1975). Model ecosystem for the evaluation of pesticide biodegradibility and ecological magnification. Environmental Science and Technology 5, 709-713.

Miller, D.R. (1979). Models for total transport. Principles of ecotoxicology scope, vol. 12. Edited by G.C. Butler. John Wiley and Son Inc. New York, NY, 71-90.

Neely W.B. *et al.* (1974). Partition coefficient to measure bioconcentration, potential of organic chemicals in fish. Environ. Sci. 'Technol. 8,1113-1115.

Nihoul, J C.J. (1984). A non-linear mathematical model for the transport and spreading of oil slicks. Ecol. Modelling 22, 325-341.

Nyholm, N. *et al.* (1984). Modelling heavy metals transport in an arctic fiord system polluted from heat transport mechanisms in lakes and reservoirs. MIT Dept. of Civil Eng., R.M. Parsons laboratory for Water Resources and Hydrodynamics. Tech. Report no. 227.

Orlob, GT. *et al.* (1980). Mathematical model for simulation of the fate of copper in a marine environment. American Chemical Society. Advances in Chemistry Series 189,195-212.

Pritchard, P.H. *et al.* (1979). System design factors affecting environmental fate studies in microcosms. In Proceedings of the Workshop: Microbial Degradation of Pollutants in Marine Environments. Edited by A.W. Bourquin and R.H. Pritchard. EPA-600/9-79-012. U.S. Environmental Protection Agency, Gulf Breeze, Fla. 251.

Schwarzenbach, R.P. and Imboden, D.M. (1984). Modelling concepts for hydrophobic pollutants in lakes. Ecol. Modelling 22, 171-213.

Seip, K.L. (1978). Mathematical model for uptake of heavy metals in benthic algae. Ecological Modelling 6, 183-198.

Stumm, W. and Morgan, J.J. (1970). Aquatic Chemistry. John Wiley and Son Inc., New York.

Thomann, R.V. (1984). Physio-chemical and ecological modelling the fate of toxic substances in natural water systems. Ecol. Modelling 22, 145-171.

Thomann, R.V. *et al.* (1974). A food chain model of cadmium in Western Lake Erie. Water Research 8, 841-851.

Turro, N.J. (1965). Molecular Photochemistry. Benjamin, New York, 18-19.

van Baaten, C. and Marler, J.E. (1966). Occurrence of hydrogen peroxide in sea water. Nature 211, 951.

Veith, G.D. *et al.* (1979). Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish Res. Board Can 36, 1040-1048.

Vereschueren, K. (1977). Handbook of environmental data on organic chemicals. Van Nostrand Reinhold, New York.

Wong, G.T.F. (1989). Photochemical Reactions. In Mathematical Submodels in Water Quality Systems. Edited by S. E. Jørgensen. Developments in Environmental Modelling 14, 195-216.

Zafiriou. O.C. and True, M.B. (1979a). Nitrite photolysis in seawater by sunlight. Mar. Chem. 8, 9-32.

Zafiriou. O.C. and McFarland, M. (1981). Nitric oxide from nitrite photolysis in the central equatorial pacific. J. Geophys. Res. 86, 3173-3182.

Zepp, P.G. and Cline, D.M. (1977). Rates of direct photolysis aquatic environment. Environ. Sci. Technol. 11, 329-366.

Zepp, P.G. (1978). Quantum yields for reaction of pollutants in dilute aqueous systems. Environ. Sci. Technol. 12, 327-329.

Zepp, P.G. and Baughman, G.L. (1978). Prediction of photochemical transformation of pollutants in the aquatic environment. In Aquatic Pollutants : Transformation and Biological Effects. Edited by O. Hutzinger *et al.* Pergamon Press, New York, 237-263.

Zepp, P.G. (1982a). Photochemical transformations induced by solar ultraviolet radiation in marine ecosystems. In The Role of Solar Ultraviolet Radiation in Marine Ecosystems. Edited by J. Calkins. Plenum Press, New York. 293-307.

Zepp, P.G. (1982b). Experimental approaches to environmental photochemistry. In The Handbook of Environmental Chemistry. Edited by O. Hutzinger, Vol. 2, Part B. Springer-Verlag, Berlin, 19-40.

Zika, R.G. *et al.* (1984). A comparison of photolysis and substitution decomposition rates of methyl iodide in the ocean. J. Geophys. Res. 11, 353-356.

CHAPTER 5

HEAVY METALS AND OTHER INORGANIC TOXIC SUBSTANCES

John Jackson

5.1 SOURCES, MOVEMENT AND SINKS

The presence of heavy metals and other toxic inorganic substances in lakes and reservoirs is attributable to both natural processes and human activities. These sources of contamination of the general environment are, for many metals and toxic substances, numerous, diverse and difficult to identify. The problem of the characterisation of sources and of subsequent fate and suitable control measures for toxic contaminant '... is one of the leading and most difficult international issues confronting environmental managers and decision makers today' (Thomas and Swain, 1988).

Metals enter lakes and rivers as a result of natural physical and chemical processes such as weathering and leaching of soils and rocks. These processes result in 'background' levels of metals in fresh waters (see, for example, a representative table in Förstner and Wittman, 1983). A study on the sediments of 74 lakes in several regions indicates that geochemical variability is low for metals such as zinc and copper and slightly higher for lead, mercury, cadmium and cobalt but that manganese, chromium and nickel are more variable (Förstner, 1977). Surface waters in certain areas have relatively high concentrations of individual elements as a result of contact with particular soils or rocks - for example high concentrations of fluoride or of selenium (Peterson, 1990, Maier *et al.*, 1988) which may be associated with health problems.

Human activities typically result in elevated levels of lead, cadmium, mercury and zinc in fresh water (Meybeck *et al.*, 1989). These and other metals are derived from a wide range of sources and transported directly or indirectly to water bodies (Figure 5.1). Mining acts to expose metal-rich ores, allowing metals to be transported from washing effluents, tailings ponds and leachates. The metals from these sources may reach ground waters, rivers or lakes in significant quantities with potentially adverse environmental effects such as those described in Buttle Lake, Canada which received metals from mining activities and which showed declines in diversity of various biotic communities (Deniseger *et al.*, 1990).

A wide range of industrial activities refine metal ores, use metals as a raw material for their products or eliminate metals as a by-product of their processes. Ferrous and non-ferrous foundries, plating and vehicle industries, chemical fertilizer and paper industries use and release a number of heavy metals such as cadmium, chromium, mercury, lead, nickel and zinc. Food processing and textiles industries produce effluents with elevated levels of heavy metals (see Table 5.1 after Klein *et al.*, 1974 in Förstner and Wittmann, 1983 for metals in industrial waste waters in New York, U.S.A.).

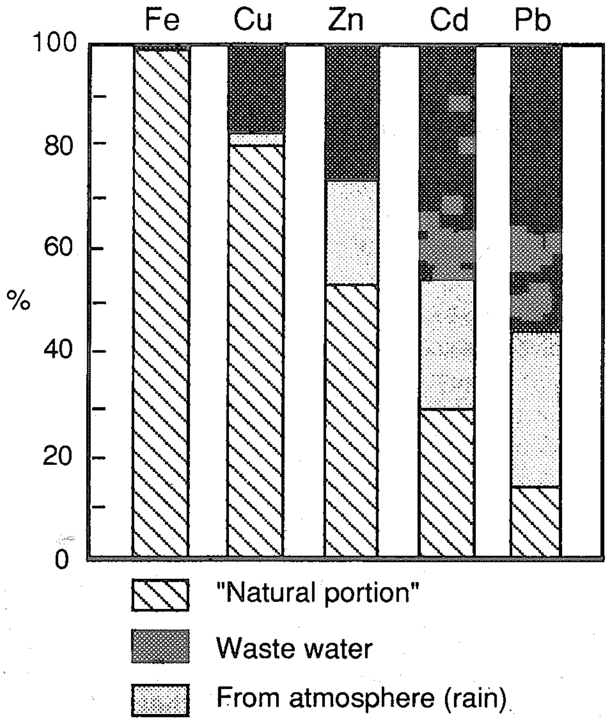


Fig. 5.1 Anthropogenic portions in the heavy metal load of a prealpine lake (Lake of Alpnach, Switzerland) from Stumm and Baccini, 1978

Table 5.1 Metals in industrial wastewaters in New York (after Klein *et al.*, 1974)

	Average concentrations in µg/l				
Industry	Cu	Cr	Ni	Zn	Cd
Meat processing	150	150	70	460	11
Fat rendering	220	210	280	3,890	6
Fish processing	240	230	140	1,590	14
Bakery	150	330	430	280	2
Miscellaneous foods	350	150	110	1,100	6
Brewery	410	60	40	470	5
Soft drinks and flavourings	2,040	180	220	2,990	3
Ice cream	2,700	50	110	780	31
Textile dyeing	37	820	250	500	30
Fur dressing and dyeing	7,040	20,140	740	1,730	115
Miscellaneous chemicals	160	280	100	800	27
Laundry	1,700	1,220	100	1,750	134
Car wash	180	140	190	920	18

Domestic waste water is the largest single source of heavy metals discharged to the environment in effluents or sewage sludges which generally contain elevated levels of copper, lead, zinc, cadmium and silver (Förstner and Wittmann, 1983). Storm water runoff in urban areas contains relatively high levels of heavy metals such as copper, lead and zinc, together with bacteria, nutrients and a high BOD. The metals will be associated to a great extent with particulates which means that metal concentrations in receiving lakes may be localized, unless the suspended particulates are transported extensively - for example in some shallow lakes (Pollman and Danek, 1988). Storm water draining directly into lakes from urban areas may exceed water quality criteria for metals but such problems are multiplied where storm water causes overflow of sewerage systems and disrupts sewage treatment through high flow. Runoff from melting snow in urban areas often contains particularly high levels of heavy metals.

Disposal by burial or discharge in soils of municipal solid wastes and industrial solid and liquid wastes is a potential source of heavy metals and other inorganic toxic substances. Whether lakes and other water bodies are contaminated with metals depends upon the type and quantity of waste, the proximity of the disposal site to water bodies, the design and operation of the site and the hydrogeology and climate in the area (Farquhar and McBean, 1988). The contaminants reach water bodies as surface runoff, leachates to ground water and, in some cases, as vapours.

Although substantial quantities of metals and other inorganic substances enter lakes directly from human and natural activity, other environmental sectors also transport them to lakes. Rivers obviously play a major role in transport of substances in solution or in association with suspended solids and act to collect discharges and metals from their drainage basins before flowing into receiving lakes. A good example is that of Lake Ontario, for which the Niagara River is the major source of mercury, lead, zinc and copper (Thomas *et al.*, 1988).

For many lakes, the atmosphere is also a significant route of transport for heavy metals and other substances entering the water body. The degree of significance will depend on the proximity of the lake to anthropogenic sources of airborne metals and on the ratio of the drainage basin area to the surface area of the lake. When a large lake has a relatively small drainage basin, a higher proportion of metals entering the lake will be derived from atmospheric sources than would be the case if the lake had a relatively large drainage basin (Murphy, 1988). Schmidtke and Andren (1984) suggest that 50% of metals entering the Great Lakes of North America enter in rainfall - a high proportion because of a low ratio between drainage basin and lake areas. Contaminants will enter the lakes either as wet deposition or as dry deposition. In the case of wet deposition, the airborne particles may act as nuclei for rain or snow and be carried down in the precipitation or may be 'washed out' of the atmosphere by falling precipitation. Dry deposition has been defined as deposition not associated with snow or rainfall (Schmidtke and Andren, 1984). Both wet and dry deposition are difficult to measure accurately over lakes, leading to considerable differences in estimates by different workers of inputs of metals from the atmosphere to individual lakes. Schmidtke and Andren (1984) cite a number of studies which give estimates for atmospheric inputs of metals to the

Great Lakes of North America. These studies employed a variety of components to estimate inputs, using emissions inventories, dispersion models and transfer efficiencies, sulphur tracers and bulk precipitation collection. The estimated inputs of cadmium, cobalt, chromium, nickel, copper, lead and zinc differed widely between papers. Schmidtke and Andren (1984) used a mass balance approach to examine inputs of metals to Lake Michigan, suggesting that a large proportion of lead, copper and zinc entering the lake came from the atmosphere (see Table 5.2). They state that insufficient supporting meteorological data and insufficient harmonization of measurement mean that considerable errors exist in attempting to calculate atmospheric inputs of metals to lakes.

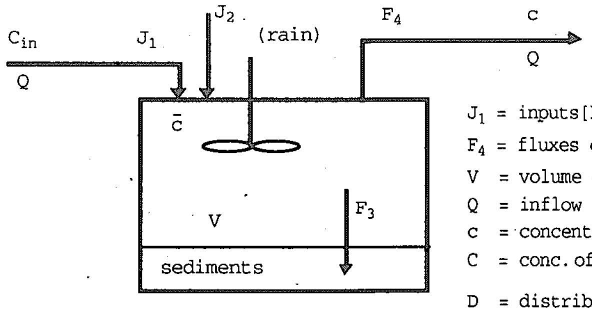
Table 5.2 Trace metal loading and sedimentation rates in Lake Michigan (tons.yr^{-1})

Element	Air	Stream	Shoreline	Sedimentation
Cr	52 - 180	78 - 250	19 - 110	330 - 500
Cu	110 - 950	73 - 180	11 - 66	160 - 270
Pb	340 - 1200	56 - 130	12 - 40	460 - 750
Zn	700 - 1000	250 - 350	50 - 440	860 - 1700

Source: Andren (1988)

Mass balance calculations can provide a useful management tool in examining inputs and behaviour of heavy metals in lakes. Their use has already been outlined in Volume I of this series (Jørgensen and Vollenweider, 1989) with reference to nutrient loadings and other inputs. Mass balance models are essentially simplified comparisons between inputs of a substance into a water body and outflows and losses of the substance from the water body. This information may be derived from field measurements or from estimates. Input information may require the compilation of source inventories, which are also of use in management for input controls (Jørgensen and Vollenweider, 1989). In addition, data or estimates of the quantities or concentrations of substances in inflowing rivers, together with inflow volumes, are required. Inputs from the atmosphere are often included. All of these data may require substantial commitments of time and may be difficult to obtain. Removal of the substance from the lake water will occur through outflowing rivers and loss to sediments. An example of a simple mass balance model for heavy metals is given in Figure 5.2 from Stumm and Baccini (1978), using data for lake volume, inflow rate (assuming that at steady state this equals outflow), sedimentation rate, concentrations in suspended matter in inflows, rainfall and particulate-water distribution characteristics.

Such models have certain assumptions - the system is at a steady state with even mixing; input flows, output flows and volume are constant and many physico-chemical and biological interactions are simplified. The possible complexities of modelling lake systems in this way are well described in Jørgensen and Vollenweider (1989). Schmidtke and Andren (1984) and Tisue and Fingleton (1984) give examples of the use of more elaborate mass balance models for heavy metals in Lake Michigan where account is taken of a wider range of environment processes, such as shoreline erosion and release from sediment. Mass balance models can provide useful comparisons of the dynamics of substance behaviour in different lakes and can be used in a number of ways in management, such as in examining lake responses to pollution control.



J_1 = inputs [kg year^{-1}]
F_4 = fluxes out [kg year^{-1}]
V = volume of lake [m^3]
Q = inflow or outflow rate [m^3 year year^{-1}]
c = concentration of soluble species
C = conc. of species in suspended matter [mg kg^{-1}]
D = distribution coefficient = $\frac{C}{c}$ [m^3 kg^{-1}]
P = sedimentation rate [kg year^{-1}]

Mass balance:

$$J_1 = QC_{in} : F_3 = CP = DcP$$
$$F_4 = QC$$
$$V\frac{dc}{dt} = J_1 + J_2 - F_3 - F_4$$
$$\frac{dc}{dt} = \frac{Qc_1 + J_2}{V} - C\left(\frac{Q + DP}{V}\right)$$
$$c(t) = C_{in} \exp\left(-\frac{Q + DP}{V}t\right) + \frac{QC_{in} + J_2}{Q + DP}\left[1 - \exp\left(-\frac{Q + DP}{V}t\right)\right]$$

At steady state:

$$t \rightarrow \infty \quad c(t) = \bar{c}$$
$$\bar{c} = \frac{QC_{in} + J_2}{Q + DP}$$

Comparison with field data in Greifensee
($V = 1.25 \times 10^8$ m^3, $Q = 8.9 \times 10^7$ m^3 year^{-1}, $P = 3.7 \times 10^7$ kg year^{-1})

Metal	C_{in} *mg m^{-3}*	*D* *kg^{-1}*	J_2 *(rain) kg year^{-1}*	$\bar{c}$ *calculated mg m^{-3}*	$\bar{c}$ *measured mg m^{-3}*
Zn	19.8	25	1316	3.1	4.1
Pb	3.2	120	1376	0.4	0.60
Cu	3.8	35	224	0.4	1.0
Cd	0.1	65	6	0.01	0.06

Fig. 5.2 Mass balance model exemplified for heavy metals in Greifensee. Data from Tschopp (1977). From Stumm and Baccini, 1978.

Considerations in using mass balance techniques can be seen to include inflow volumes, outflow volumes and total lake volume which are often used to calculate a water residence time - the time taken to replace all of the water in the lake. However, water residence time is not always a significant factor in the persistence of heavy metals in the water column and a distinction may be made between residence time of a substance in the water and residence time of water in the lake (Murphy, 1988). The substance residence time in the water column will be related to loading rates and removal rates and to physical, chemical and biological conditions which will differ considerably between lakes.

Transport and distribution of heavy metals are dependent on the sum of characteristics of the lake in question and on the nature of the contaminants. The location of sources and the chemical and physical character of effluents, inflowing rivers and runoff, with the chemical and physical character of the lake, will determine concentrations, partitioning and speciation, sedimentation and resuspension, redox and chemical reactions and biological mediation. The physical and chemical form of the substance will help determine which transport processes are most important in its movement, distribution and ultimate fate.

The limnological processes of circulation, stratification and mixing play an important role in the distribution of substances in lakes. Inflowing rivers create currents which continue the movement of toxic metals in the lake. Thomas *et al.* (1988) produced a case study of contaminants in Lake Ontario in which a 'plume' of sediment was identified in the lake, derived from the Niagara River and contaminated with mercury. They note that many metals are associated with suspended or settled particulates. In the case of lead, however, the identification of particular sources and subsequent current transport was not possible - the atmosphere is a significant pathway for lead, leading to deposition over the whole lake surface. Thomas *et al.* (1988) identified higher concentrations of lead in deeper water sediments - the lead was associated to a greater extent with finer particles which were carried longer distances by currents. They also suggested that thermal stratification of the lake leads to a more rapid surface water transmission of metals from inflow to outflow. It may be seen that transport of toxic metals and other substances in a lake is dependent upon sources, particulate and sediment characteristics, currents and mixing - in summary, a complex system where the range of processes and the time-lag involved make it difficult to link sources with eventual distribution without extensive study.

The chemical form of metals and other inorganic substances is of great importance in determining their behaviour and impact and may in certain conditions be manipulated through management to influence distribution and effects.

Speciation of metals is of special significance for biological availability and toxicity - different chemical species of the same element may have quite different biological effects.

Complexation of metals with inorganic and organic ligands is of importance in transforming metals in lakes. Ions such as sulphate and chloride play a role in determining the concentration of free metal ion in the water - the strength of binding is different for different metals. Organic substances in fresh water may be grouped into three main categories (Stumm and Baccini, 1978):

1. Low molecular weight organic substances such as amino acids, sugars and other molecules;

2. Organic polymers such as polypeptides, lipids, poly- saccharides, fulvic and humic acids;

3. Organic colloids, either as high-molecular weight compounds or as organic compounds sorbed or bound to inorganic colloids.

Metals also bind strongly to hydrous oxides of Al(III), Si(IV), Fe(III), Mn(III, IV), binding for these and for some organic substances being of forms such as:

$$\equiv ROH + Me^{2+} \rightleftharpoons \equiv ROMe^{+} + H^{+}$$

$$2 \equiv ROH + Me^{2+} \rightleftharpoons (\equiv RO)_2Me + 2H^{+}$$

(Stumm and Baccini, 1978).

The complexing and binding of metals in the ways described mean that significant amounts of metal in a lake will be in association either with dissolved organic matter or with organic or inorganic particulates. This will have a bearing on biological availability and, in the case of particulates, on transport.

Förstner and Wittmann (1983) compare the significance of the different sinks for heavy metals in natural aquatic systems, identifying complexation and flocculation with organic matter, coprecipitation with hydrous iron and magnesium oxides and uptake by biota as being of particular importance for sediment association of heavy metals. Sedimenting phytoplanktonic material and biogenic particles to which heavy metals are bound are of significance in the movement of metals to sediment sinks. The complexing and adsorption processes outlined above tend to associate metals with particulates, which then settle, leading to an accumulation of metal in sediment. Once in the sediment, redox reactions are of importance in determining the mobility and form of heavy metals and other toxic substances - however, the redox state of the water and of the sediment may lead to the release of metals from particulates, renewed availability to biota and the potential for movement in the lake system. This is the case in reducing environments for iron and manganese which are the major metals involved in redox processes (Stumm and Baccini, 1978). For cadmium, copper, nickel, lead and zinc, however, reducing environments serve to immobilize the metals as insoluble sulphides (Jørgensen, 1980). Most redox reactions tend to be biologically mediated by microorganisms in lakes (Stumm and Baccini, 1978). Reducing environments in sediment and especially in the hypolimnion are of concern for management not only because of mobilization of iron and manganese but because of the production of toxic hydrogen sulphide, with consequent effects on water quality. Agget and Kriegman (1988), describe the redox-related mobilization of arsenic from sediments in Lake Ohakuri, a hydroelectric reservoir in New Zealand. In oxidizing conditions, As (V) is adsorbed onto Fe(III) hydroxides but when thermal stratification develops, with lowering of the oxygen concentration in the hypolimnion, surface sediment Fe(III) is reduced to Fe(II), with a release of arsenic to interstitial water and the hypolimnion as the more toxic As(III).

Movement of metals back into the water column from sediment sinks may also occur as a result of sediment resuspension by physical influences (currents, waves), biological action (benthic animals) or human action (dredging, boat activities).

Sediment as a sink for metals has provided useful information for many lakes on historical trends in metal inputs through the analysis of sediment cores. An obvious condition for the use of sediment as a record in this way is that the metals should not be mobile (as are, for example, iron and manganese, in reducing conditions). Dating of sediment cores is frequently done by analysing isotope decay (^{210}Pb, ^{137}Cs, $^{239+240}$Pu) or by identifying visible annual or seasonal layering in the cores (Alderton, 1985). The analysis of trends in cores indicate general correlation of sediment metal levels with historical trends in use (Figure 5.3) or release of the metals by humans but complicating factors (such as metal mobility in certain redox conditions or bioturbation) require a cautious approach to interpretation of trends.

Biota are central to the study and control of heavy metals and other inorganic toxic substances in lake systems. Microbes, plants and animals all play significant roles in determining the transport, chemical form and transfer to sites of metals but the most important factor is that of the effects of such substances. Of ultimate concern is the eventual transfer of toxic substances through water or food to humans and the resulting health effects. However, human uses of lakes are heavily dependent upon biological systems in maintaining water quality and in providing food or usable biomass.

Transport of metals in lake systems will be influenced by uptake or adsorption by biota, binding to particles of biogenic origin or complexing by dissolved organic matter, especially that of plant origin. The transfer to, and storage in, sediment sinks will be influenced by settling of biological particles with which metals are associated (such as dead phytoplankton cells or zooplankton faeces) and biological action in sediments (such as bioturbation or microbial action which change mobility).

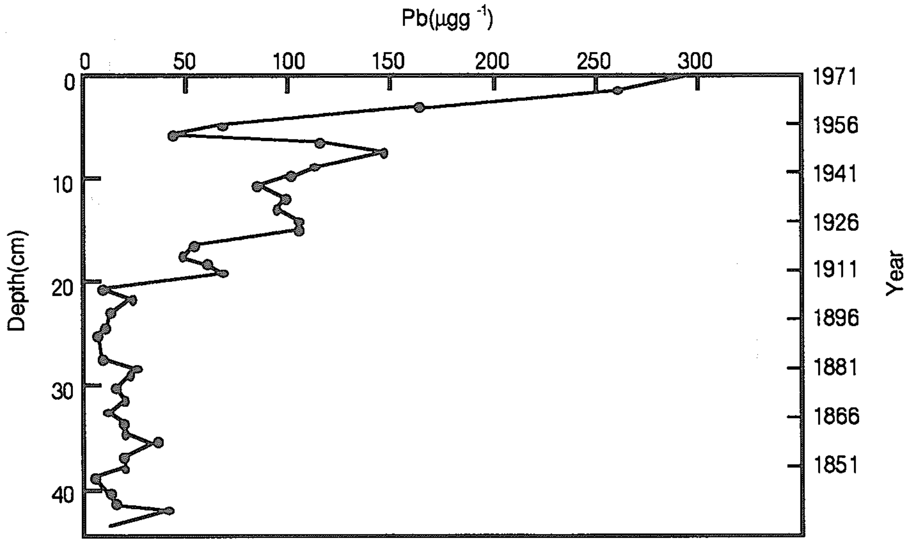


Fig. 5.3 Profile of Pb in a core from Evergreen Point Bridge, Lake Washington (after Barnes and Schell 1973). From Alderton, 1985.

The effects and uptake of metals in biota are well documented elsewhere and little more than an outline is presented here. Toxicity of metals and other inorganic substances will depend upon a number of factors which influence the availability of the substance to the organism. The concentration of the metal ion is a basic factor - not necessarily in absolute terms because different chemical forms will have different availabilities, depending on how uptake occurs. The chemical form will depend, as described above, on source and on interactions with dissolved molecules and with particles. Other water quality factors will not interact directly with the metal, but may influence uptake. For example, cadmium is more toxic to algal species in soft water (20mg l^{-1} $CaCO_3$) than in hard water (300mg l^{-1} $Ca\ CO_3$) because of antagonism between uptake of calcium or magnesium and cadmium (Munawar *et al.* 1988). Munawar *et al.* (1988) group the effects of contaminants upon algae as follows:

1. Community structure responses - changes in size and species composition.

2. Physiological / anabolic responses - related to biomass production with possible effects on food chains.

3. Ultrastructural responses.

Figure 5.4 gives an indication of the physiological effect of metals on phytoplankton, showing decreased carbon assimilation (primary production) with the addition of metals.

Similar effects of reduction in biomass production have been observed in zooplankton and zoobenthos as a result of exposure to heavy metals, both in terms of growth and of reproduction (Hodson *et al.* 1984, Eadie *et al.* 1988) but there are considerable difficulties in working with natural communities and in identifying the effects of heavy metals or other substances as phenomena distinct from natural fluctuations. Many of the effects for biota have been observed in the laboratory. Sublethal effects of heavy metals on fish are well described as a result of laboratory studies; field work on direct responses to metal pollution being time-consuming and complex. However, observations of tissue concentrations in natural populations are made in many cases and in these samples, the levels of hepatic metallothionein may be used as an indicator of 'unsafe' degrees of metal exposure (see for example, Deniseger *et al.* 1990).

An issue which has received recent attention has been the accumulation of mercury by fish in lakes. The major form of mercury in fish is methylmercury, the formation of which (primarily by micro-organisms) is influenced by various complex factors but which is enhanced by low pH. Methylmercury is transferred along lake food chains (Stokes and Wren, 1987) and levels in fish have reached levels of concern in acidified lakes in Sweden - the mercury reaching these remote lakes and leading to levels of concern is derived primarily from atmospheric sources. Similar elevations in fish methylmercury have also been observed in north American reservoirs, where the source of mercury is suggested as flooded soils and vegetation (Stokes and Wren, 1987).

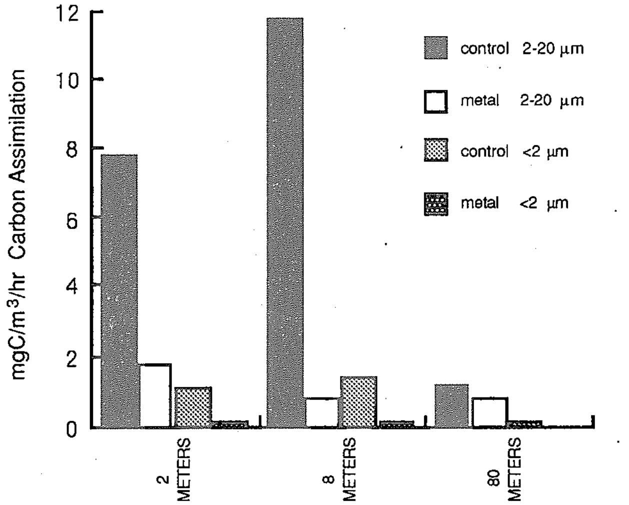


Fig. 5.4 Effects of metal mixture additions in algal size fractions at different depths in Lake Ontario during a stratified period July, 1983. From Munawar *et al.* (1988)

5.2 MANAGEMENT

The management of heavy metals and other toxic substances in lakes is combined in practice with the management of other problems (for example, eutrophication associated with phosphate inputs) as part of an integrated approach to water quality. The various influences on behaviour and effects of such substances indicate the complexity of metal interactions in lakes and the difficulty of drawing up practical management strategies for control. As stated above, models such as mass balances aid in understanding the structure of the lake system and in estimating the effectiveness of management action. Residence time models which use physical and chemical data are of use in predicting the behaviour of toxic metals in lakes - the time that any given input takes to be flushed from the system or immobilized in sediments. Metal behaviour in the environment is more complex than that simulated by the model but options for disposal and capacities for 'self-cleaning' can be investigated in this way (Honeyman and Santschi, 1988). These models will aid in estimation of likely environmental concentrations. This may be taken further to model interactions between the substance and biota - uptake and excretion, toxicity and food chain transfer (Jørgensen, 1980) which allows the likely effects of inputs of toxic substances to be predicted to some degree. The difficulty of modelling a system which is not at steady state makes prediction, likely concentrations and effects subject to uncertainty. Thomas *et al.* (1988) draw attention to the difficulty of associating observed effects with particular contaminants in a complex lake system. They suggest that for highly persistent substances (such as heavy metals) the lag time between input and effects may be so long as to prevent effective management action. They go on to state that 'given the persistence of many of these substances, the old notion of *assimilative capacity* used for traditional parameters such as phosphorus, BOD, etc., is clearly *passé*. This has extremely important implications for future management and control strategies'.

Management of hazardous substances may be aimed at preventing environmental problems occurring - a pro-active approach - or at reducing the scale of an existing problem - a reactive approach. Jørgensen (1980) classified restoration methods for lakes into two groups:

1. Reduction of external loading;

2. Intervention in the lake ecosystem.

Reduction of external loading may be summarized as being various options (such as source control) which are not uniquely used for lakes but which may be effective in restricting inputs of heavy metals and other toxic substances to all surface and ground waters, together with other environmental compartments. At a basic level, a management decision may be made on whether to permit use of the substance. Such a decision is usually made at governmental level, in light of the environmental behaviour, distribution and effects of the substance, often including comprehensive hazard and risk assessments with reference to possible environmental damage and human exposure. Bans on use are relatively rare. More generally, some restriction may be applied through land use planning controls for industrial activities or through controls on certain processes or types of use. The most widespread form of control is exerted through standards for concentrations of metals in effluents or receiving waters. This may have an influence on process or activity or may dictate the level of treatment of the effluent required before discharge. Treatment may remove substances from waste water for subsequent alternative disposal or there may be some incentive to recover and reuse certain metals. Lastly, external loadings to lakes may be controlled through waste management - contaminated wastes may only be stored or disposed of in certain ways. An obvious difficulty exists in the control of metals and other inorganic substances from diffuse sources - treatment is often difficult but use control may still be an option - for example, the restriction of the use of lead in motor fuel.

Treatment of waste waters to remove metals and inorganic substances has various degrees of complexity and efficiency. In practice, the treatment technique is chosen according to the character of the effluent, the cost of the technique and the required standard of effluent for discharge. Reviews of the general principles and techniques of treatment are given by Förstner and Wittmann (1983) and Clifford *et al.* (1986). At the most basic level are various methods of precipitation such as coagulation with iron salts or aluminium sulphate. More advanced techniques use ion exchange or adsorption (with resins, activated carbon or activated alumina) or membrane processes (reverse osmosis and electrodialysis). Treatment obviously does not eliminate metals - they are removed from high-volume waste waters and converted to more easily handled forms such as sludges which still require disposal - effectively transferring the problem. Jørgensen (1980) points out that diversion of contaminated waste waters to rivers or the sea may well be a management option in certain cases to avoid environmental problems in lakes. In routine biological treatment of sewage, high concentrations of heavy metals may inhibit the increase of microbial biomass and lead to a reduction in efficiency of both aerobic and anaerobic processes.

The difficulty of dealing with periodically high concentrations of heavy metals in urban stormwater runoff was outlined above. Oberts and Osgood (1991) describe the use of detention ponds and wet marshes in reducing total lead by over 90% in stormwater entering an urban lake in Minnesota, U.S.A., primarily through the settling of solids to which much of the lead was bound. Similar settling techniques are used for mine wastes but efficiency may not always be sufficient to meet standards and other options may need to be used, such as more advanced physical or chemical treatment before discharge.

Waste management has a significant role to play in the control of entry of metals and other toxic substances to lakes. As a first step, the encouragement of reuse, recycling and recovery will reduce quantities of wastes. Thomas and Swain (1988) list a number of aspects of waste control, starting with industrial process selection. Waste treatment, destruction and disposal are best carried out on-site or near the source to minimize hazards associated with transport and accidents in handling but centralized waste treatment should be organized for smaller waste generators. Waste treatment plants should be effectively operated, new techniques encouraged and technology transfer instituted where possible. The management of disposal sites is of great importance in controlling contamination of lakes - the design of the dump site base and cover may act to reduce infiltration and discharge (Farquhar and McBean, 1988). The initial planning of the site for the dumpsite will be one of the factors in determining whether wastes will enter the hydrological cycle, as will the choice of the type of waste permitted for disposal.

The second category of lake restoration methods listed by Jørgensen (1980), was intervention in the lake ecosystem. Again, it should be emphasized that the management of heavy metals and other toxic substances will be performed in parallel with the management of other water quality influences. The selection of techniques is not always as straightforward as it might appear, therefore, because techniques to improve water quality in response to one influence may have no effect or an adverse effect with respect to another influence - the characteristics of the lake will be of great importance in determining the effectiveness of techniques chosen.

Aeration of lakes can be used where anoxia in the sediment or hypolimnion is allowing movement of iron and manganese into the water column, with consequent effects on water quality. In practice, the immobilization of metals will be only one aim of aeration; the prevention of sulphide formation, inhibition of blue-green algal blooms, elevation of oxygen to prevent fish kills and reduction of internal phosphate cycling being others. At the most simple level is circulation of the entire water column to prevent thermal stratification. This technique can control accumulation of metals in the water of some lakes but has the disadvantages of reducing transparency, eliminating cold water habitats and ruling out depth-selective withdrawals (Kortmann *et al.* 1988). The circulation is executed by using pumps or bubbled air which act to move hypolimnion water to the surface. More advanced techniques aerate specific layers of lake water, without disrupting thermal stratification. The hypolimnion may be aerated by pumping water to the surface, whereby it is aerated, before it is diverted immediately back to the hypolimnion. Alternatively, aeration may take place directly in the hypolimnion using bubbled air (Jørgensen, 1980). Kortmann *et al.* (1988) describe the use of fine bubble diffusers to aerate specific layers in thermally stratified water to improve water quality at mid-depth for selective offtake. In this case, the water quality of the upper levels of a reservoir were affected by high algal populations, while the middle and lower layers were oxygen-deficient (resulting in high levels of iron (II) (9 mg l^{-1}) in solution) and, near the sediment, contained high levels of suspended solids. The bubble diffusers were used to aerate the middle layers of water, causing a reduction in iron (II) and making the water suitable for depth-selective abstraction. Similar techniques are possible in certain cases for sediment aeration (Jørgensen, 1980).

Sediment removal is used to reduce the releases of accumulated metals and phosphorus unto the water column. This method may be quite effective as a means of reducing the reservoir of toxic substances but has disadvantages, among them being high cost. Sediment is removed by dredging, which has the disadvantage of resuspending sediment - risking secondary pollution of the water column - and temporarily destroying benthic communities (Cooke *et al.* 1986). Conventional grab bucket dredges cause considerable resuspension of sediment but this can be contained in the immediate vicinity of dredging using a silt curtain - a buoyed polythene sheet of the same depth as the water and weighted along the bottom edge. Grab buckets have a poor pick-up capacity for flocculated particles. Hydraulic dredges with cutter heads also have the disadvantage of resuspending considerable quantities of sediment. Cooke *et al.* (1986) describe more specialized water lift pumps which reduce turbidity and which increase the solids content of the dredged material (resulting in fewer volume problems for disposal). The cost of equipment and time involved limit the use of dredging to relatively small and highly contaminated areas, such as harbours. Disposal of dredged sediment presents further problems - the sediment contains relatively high levels of heavy metals or toxic substances which must be prevented from contaminating other parts of the environment from the dump site (such as ground waters). The dredge spoils frequently have a high water content which may need to be reduced before disposal.

Stokes and Wren (1987) give a brief review of intervention methods for mercury-contaminated sediments in lakes and rivers. In addition to dredging, some examples of covering contaminated sediment with clay or sediment to reduce movement of mercury from the sediment to the water column. They also give some examples of action to prevent formation of the more biologically available methylmercury but there is no indication of such methods being in widespread use.

Intervention techniques may be useful options for remedial action but can be of limited effectiveness in the long-term without source control. For example, dredging contaminated sediment from a lake may remove internal sources of heavy metals, but if external loadings of heavy metals which contaminate sediment are not reduced, dredging will have to be repeated.

Effective management of heavy metals and inorganic toxic substances requires both the extension of pollution control beyond the boundaries of the lake and integration of techniques and priorities to enable management of these substances as one among many aspects of water quality control. This in turn demands co-operation between various organizations in the drainage basin and a unified perception of the lake system and its surrounding environment. This is what ecosystems approaches to management aim to do and although such an approach by definition is not restricted to the lake or heavy metals control, it provides a framework within which effective management should be possible. Hartig and Vallentyne (1989) describe the ecosystems approach as taking account of the interaction between economic, social and environmental interests, all of which are essential to human activity within the whole ecosystem. This approach aims at an integration of knowledge, allows systems at different levels of integration to be related to one another and advocates actions which are ecological, anticipatory and ethical with respect to the environment (Hartig and Vallentyne, 1989).

The ecosystems approach may be seen in co-operation over management of the Great Lakes of North America. Earlier co-operation between Canada and USA under the Great Lakes Water Quality Agreement (GLWQA) led to basin-wide control of phosphorus to reduce eutrophication. More recently, an ecosystems approach has been used in the development of restoration plans for 42 degraded areas (Hartig and Vallentyne; Hartig and Thomas, 1988). In many of these areas, heavy metals are a significant problem in contaminated sediments. The remedial action plans define the problems and identify impairment of use, causes and pollutant sources. Remedial actions are proposed to restore beneficial use and schedules for implementation, responsibility, evaluation of progress and public consultation proposed. Not all lake management strategies will be as complex (or expensive) as this but such approaches illustrate the benefit of setting lake management of heavy metals in a wider human and environmental context.

REFERENCES

Agget, J. and Kriegman, M. R. 1988 The extent of formation of Arsenic (III) in sediment and its release to hypolimnetic waters in Lake Ohakuri. *Wat. Res.* 22(4), 407-411.

Alderton, D. H. M. 1985 Sediments. In: *Historical Monitoring* prepared by Monitoring and Assessment Research Centre (MARC), King's College London, The Old Coach House, Campden Hill, London, U.K.

Andren, A. W. 1988 Transfer of toxic substance at the air/water interface: the Great Lakes. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol III, Sources, fate and controls of toxic contaminants, pp. 225-236, Lewis Publishers, Chelsea, Michigan.

Clifford, D. Subramonian, S. and Sorg, T. J. 1986 Removing dissolved inorganic contaminants from water. *Environ. Sci. Technol.*, 20(11), 1072-1080.

Cooke, G. D., Welch, E. B., Peterson, S. A. and Newroth, P. R. 1986 Lake and reservoir restoration, Butterworths, Boston.

Deniseger, J., Erickson, L. J., Austin, A., Roch, M. and Clarke, M. J. R. 1990 The effects of decreasing heavy metal concentrations on the biota of Buttle Lake, Vancouver Island, British Columbia. *Wat. Res.*, 24(4), 403-416.

Eadie, B. J., Nalepa, T. F. and Landrum, P. F. 1988 Toxic contaminants and benthic organisms in the Great Lakes: Cycling, fate and effects. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol I, Chronic effects of toxic contaminants in large lakes, pp. 161-178, Lewis Publishers, Chelsea, Michigan.

Farquhar, G. J. and McBean, E. A. 1988 Disposal activities as a source of contaminants to large lakes. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol III, Sources, fate and controls of toxic contaminants, pp. 61-82, Lewis Publishers, Chelsea, Michigan.

Förstner, U. 1977 Metal concentrations in recent lacustrine sediments. *Arch. Hydrobiol.*, 80, 172-191.

Förstner, U. and Wittmann, G. T. W. 1983 Metal Pollution in the Aquatic Environment, 2nd edition. Springer-Verlag, Berlin.

Hartig, J. H. and Thomas, R. L. 1988 Development of plans to restore degraded areas in the Great Lakes. *Environmental Management*, 12(3), 327-347.

Hartig, J. H. and Vallentyne, J. R. 1989 Use of an ecosystem approach to restore degraded areas of the Great Lakes. *Ambio*, 18(9), 423-428.

Hodson, P. V., Whittle, D. M., Wong, P. T. S., Borgman, V., Thomas, R. L., Chan, Y. K., Nriagu, J. O. and Hallet, D. J. 1984 Lead contamination of the Great Lakes and its potential effects on aquatic biota. In: Nriagu, J. O. and Simmons, M. S. (*Eds.*), *Toxic contaminants in the Great Lakes*, pp 335-369, Wiley-Interscience, New York.

Honeyman, B. D. and Santschi, P. H. 1988 Metals in Aquatic Systems. *Environ. Sci. Technol.*, 22(8),862-871.

Jørgensen, S. E. 1980 Lake Management (Water development, supply and management, volume 14). Pergamon, Oxford.

Jørgensen, S. E. and Vollenweider, R. A. (*Eds.*) 1989 Guidelines of Lake Management. Volume I Principles of Lake Management, ILEC/UNEP, Shiga-Kaikan Build, 3-4-22 Kyomachi, Otsu, Shiga 520, Japan.

Kortmann, R. W., Conners, M. E., Knoecklien, G. W. and Bonnel, C. H. 1988 Utility of Layer Aeration for Reservoir and Lake Management. *Lake and Reserv. Mange.*, 4(2), 35-50.

Maier, K. J., Ogle, R. S. and Knight, A. W. 1988 The selenium problem in lentic ecosystems. *Lake and Reserv. Manag.*, 4(2), 155-163.

Meybeck, M., Chapman, D. V. and Helmer, R. 1989 Global Freshwater Quality: A First Assessment. WHO/UNEP. Blackwell Reference, Oxford.

Munawar, M., Wong, P. T. S. and Rhee, G.-Y. 1988 The effects of contaminants on algae: an overview. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol I, Chronic effects of toxic contaminants in large lakes, pp. 113-160, Lewis Publishers, Chelsea, Michigan.

Murphy, T. J. 1988 Significance of atmospheric inputs of toxic materials to large lakes. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol III, Sources, fate and controls of toxic contaminants, pp. 83-96, Lewis Publishers, Chelsea, Michigan.

Oberts, G. L. and Osgood, R. A. 1991 Water-quality effectiveness of a detention/wetland treatment system and its effect on an urban lake. *Environmental Management*, 15(1), 131-138.

Peterson, P. J. 1990 Chemical etiology of endemic diseases: A global perspective. In: Sandhu, S. S. *et al.* (*Eds.*). *In situ evaluations of biological hazards of environmental pollutants*, pp. 195-201. Plenum Press, New York.

Pollman, C. D. and Danek, L. J. 1988 Contribution of urban activities to toxic contamination of large lakes. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol III, Sources, fate and controls of toxic contaminants, pp. 25-40, Lewis Publishers, Chelsea, Michigan.

Schmidt, J. A. and Andren, A. W. 1984 Deposition of airborne metals into the Great Lakes: An evaluation of past and present estimates. In: Nriagu, J. O. and Simmons, M. S. (*Eds.*), *Toxic Contaminants in the Great Lakes*, pp. 81-103. Wiley-Interscience, New York.

Stokes, P. M. and Wren, C. D. 1987 Bioaccummulation of mercury by aquatic biota in hydroelectric reservoirs: a review and consideration of mechanisms. In: Hutchinson, T. C. and Meena, K. M. (*Eds.*), *Lead, Mercury, Cadmium and Arsenic in the Environment, SCOPE* report 31, pp. 225-277. John Wiley and Sons, Chichester.

Stumm, W. and Baccini, P. 1978 Man-made chemical perturbations in lakes. In: Lerman, A. (*Ed.*). *Lakes - chemistry, geology, physics*, pp. 91-126. Springer-Verlag, New York.

Thomas, R. L. Gannon, J. E., Hartig, J. H., Williams, D. J. and Whittle, D. M. 1988 Contaminants in Lake Ontario - A Case Study. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol III, Sources, fate and controls of toxic contaminants, 327-388, Lewis Publishers, Chelsea, Michigan.

Thomas R. L. and Swain, W. R. 1988 Session Summary: Sources, fate and controls of toxic contaminants. In: Schmidtke, N. W. (*Ed.*) 1988 *Toxic contamination in large lakes*, Vol III, Sources, fate and controls of toxic contaminants, pp. 1-6, Lewis Publishers, Chelsea, Michigan.

Tisue, T. and Fingleton, D. 1984 Atmospheric inputs and the dynamics of trace elements in Lake Michigan. In: Nriagu, J. O. and Simmons, M. S. (*Eds.*). *Toxic contaminants in the Great Lakes*, pp. 105-125. Wiley-Interscience, New York.

CASE STUDY

HEAVY METALS IN LAKE BALATON

J. Salánki and I. Licskó

Lake Balaton is located at the western part of Hungary. The water surface is 596km^2 with an average depth of 3.2m and a catchment area of 5775 km^2. Land use around the lake is mainly agricultural. Industry is not a significant land use (with the exception of a chemical factory). The local population in towns and villages in the lakeside communities is around 130,000. Tourism in the summer takes this figure to 800,000 people. Road and rail traffic in the vicinity of the 210km lakeshore is rather heavy (using mostly unleaded petrol). There is also an active cruise industry on the lake. Waste deposits close to the shore or in the vicinity of inflow waters are also sources of pollution, as is pollution of atmospheric origin.

Heavy metals are the most significant toxic substances in Lake Balaton. Between 1980 and 1990 regular sampling and measurement of Hg, Cd, Pb, Cu, Zn and Ni concentrations were taken from the water, sediment and aquatic animals at 5 points in the lake and at 15 main tributaries close to the inflow (Fig. 1).

Measurements were made by atomic absorption spectro-photometry as described in Salánki *et al.*, 1982. Values are given for the water in µg/1, for the sediment and animals in mg/kg dry weight. Only mean values of more than 6 samples collected in different months of the year are included in the tables, detailed data are available in research papers and reports (see references).

1. METAL CONCENTRATIONS IN THE WATER OF LAKE BALATON AND MAIN TRIBUTARIES

Soluble metal concentrations were far under permissible levels for drinking water at all locations investigated during 1988-89 as shown in Table 1. This is true even for places where metal concentrations were higher than the average (as indicated separately under "b").

2. METAL CONCENTRATIONS IN THE SEDIMENT

The level of heavy metals in the sediment was 100-10,000 times higher than in the water, however, this represents total concentrations, including insoluble metal compounds (Table 2). The metal content of the sediment is indicative of the degree of pollution. It serves as a source for solubilzation into the water depending on physico-chemical circumstances (pH, etc.) and for uptake by benthic organisms.

In some places extremely high or unusually low concentrations were detected (indicated separately with reference to sampling locations).

3. METAL CONCENTRATIONS IN THE ZOOPLANKTON OF THE LAKE

Zooplankton was collected from the open water of the lake at five locations (Fig. 1). The metal concentration was 3-4 times higher in the zooplankton than in the water, indicating a high degree of accumulation Table 3). It is remarkable that the concentrations of Hg and Pb decrease from west to eastern locations, Cu and Zn were nearly at the same level at each location, Cd varied without any rule while Ni concentrations were not detectable.

4. METAL CONCENTRATIONS IN FISH COLLECTED FROM MAIN TRIBUTARIES OF LAKE BALATON

Heavy metal concentrations in fish varied within a wide range (Table 4), however no dramatic differences were found between sampling locations. Nevertheless, in some sampling places comparatively high or low concentrations were measured. Comparison of these results with data obtained for the sediment shows that the inflow waters represented by locations E5, E6 and D2 can be considered as massive sources of metal pollution.

A more detailed analysis of data indicates that among fish organs the concentrations of some heavy metals are rather diverse: Cu is accumulated better in liver than in the gill or muscle, while Zn and Ni accumulation is much higher in the gill than in the liver or muscle. Our separate studies proved that snails accumulate better Pb than fish organs, but they are poor accumulators for Zn as compared to fish gills. In monitoring heavy metal pollution the best accumulating animals and/or organs can be recommended as biological indicators.

5. CONCLUSION

The heavy metal pollution of Lake Balaton and its tributaries is not "significant". It does not endanger aquatic life and does not hinder the use of drinking or irrigation. However, toxic metal content in the sediment is remarkable at some locations, a result of point pollution sources in the environment.

Concentrations of heavy metals in animals are low, nevertheless, if they are released from storage organs they can alter significantly basic physiological processes.

Finally there is a need to study the occurrence and concentrations of other toxic substances in the lake and its environment.

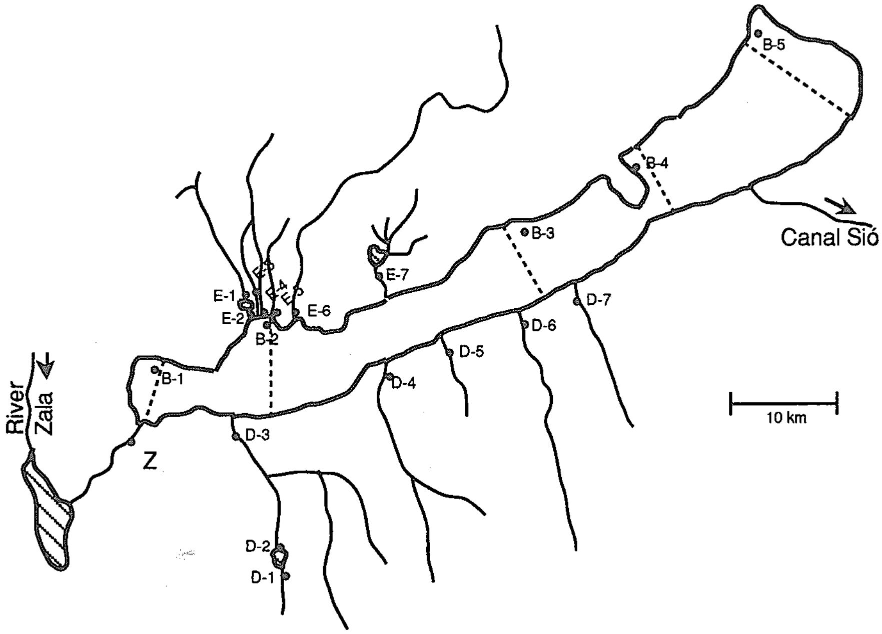


Fig. 1. Lake Balaton and sampling locations for heavy metal monitoring. E1-7: northern tributaries; D1-7: southern tributaries; Z-sampling location at River Zala; B-5: sections for sampling locations in the open water of Lake Balaton.

Table 1 Heavy metal concentrations in the water of Lake Balaton and main tributaries (µg/l)

	Hg	Cd	Pb	Cu	Zn	Ni
a	< 0.1	0.01-0.2	0.1-1.0	0.3-4.6	0.5-5.4	0.5-3.5
b		0.5-0.6	1.9-3.8	10.5	10.0-47.7	
		E7,D1	E2,D1,D3,	D7	at most places in October	

a: minimum and maximum mean values
b: markedly higher values with reference to sampling locations, according to Fig. 1.

Table 2 Heavy metal concentrations in the sediment of Lake Balaton and main tributaries (mg/kg dry weight)

	Hg	Cd	Pb	Cu	Zn	Ni
a	0.03-0.38	0.4-3.5	10.2-92.6	7.0-88.0	18.0-124.0	13.6-47.6
b	0.5-0.8	4.1-4.9	250.0		220-222	
	D1,B5	E4,E5,	E4		E1,E5	
c		0.03-0.08	2.8-8.0	1.4-3.4	8.0	1.0-2.8
		D2,B1	D2,D3	D2,D3	D2	D2

a: minimum and maximum mean values
b: markedly higher values
c: markedly lower values, with reference to sampling locations, according to Fig. 1.

Table 3 Heavy metal concentration in the zooplankton collected in the open water of Lake Balaton.

Hg	Cd	Pb	Cu	Zn	Ni
0.04-0.23	0.7-2.2	9.9-22.5	11.0-17.6	70.1-99.2	not detectable

(mg/kg dry weight, minimum and maximum mean values.)

Table 4 Heavy metal concentrations in liver, gill and muscle of fish (Esox lucius L.) collected in main tributaries of Lake Balaton (mg/kg dry weight)

	Hg	Cd	Pb	Cu	Zn	Ni
Liver						
a	0.4-0.7	1.0-4.4	1.7-5.9	11.8-37.1	95.7-187.0	2.7-8.3
b	1.3-3.6	6.1	13.5-15.0			
	D1,D5	E7	E1,E7			
c	0.03-0.08					
	E4,D2,D3,D4,					
Gill						
a	0.1-0.8	2.0-10.0	0.7-9.9	1.0-10.1	784.0-1458.0	8.6-33.7
b			17.8-51.0	21.4		
			D1-7	E1		
c						2.7
						E6
Muscle						
a	0.3-0.7	1.1-3.1	1.3-6.2	0.3-2.8	17.7-39.0	2.3-8.5
b	1.1-1.5		8.5-10.9	4.2-6.6		
	E1,E6,E7,D1,		D2,D3,D4,D7,	E5,E7		

a: minimum and maximum mean values
b: markedly higher values
c: markedly lower values with reference to sampling locations according to Fig. 1.

REFERENCES

Müller, G. 1981. Heavy metals and nutrients in sediments of Lake Balaton, Hungary. Environmental Toxicology Letters, 2 39-48.

Licskó, I. 1990. Quantitative determination of heavy metals loading Lake Balaton. Research Report, Water Resources Research Center (VITUKI), Budapest, pp.1-40.

Salánki, J. 1989. Bioindicators in monitoring heavy metal pollution in Lake Balaton and its catchment area. In: Symp.Biol.Hung. 38. Conservation and Management of Lakes (*Eds.* J. Salánki and S. Herodek) Akadémiai Kiadó, Budapest. Pp. 261-271.

Salánki, J., Z. Mastala, Katalin V.-Balogh and I. Varanka 1990. Occurrence of toxic heavy metals at the catchment area of Lake Balaton and selection of bioindicator species. Research Report, Balaton Limnological Research Institute, Tihany, pp.1-20, (in Hungarian).

Salánki, J., Katalin V.-Balogh and E. Berta 1982. Heavy metals in animals of Lake Balaton. Water Research 16 1147-1152.

V.-Balogh, Katalin, D.M. Salabarria-Fernandez and J. Salánki. 1988. Heavy metal concentrations of Lymnaea stagnalis in the environs of Lake Balaton (Hungary). Water Research 22 1205-1210.

V.-Balogh, Katalin and J. Salánki 1984. Use of zooplankton for evaluation of the heavy metal pollution of Lake Balaton. J. Hidrobiol. Moscow, 20 56-64 (in Russian).

V.-Balogh, Katalin and J. Salánki 1987. Biological monitoring of heavy metal pollution in the region of Lake Balaton (Hungary). Acta biol.hung 38 13-30.

V.-Balogh, Katalin, J. Salánki and I. Varanka 1989. Heavy metals in freshwater organisms. In: Symp.Biol.Hung. 38. Conservation and Management of Lakes (*Eds.* J. Salánki and S. Herodek). Akadémiai Kiadó, Budapest, pp.281-289.

CHAPTER 6

ORGANIC PESTICIDES IN AQUATIC ENVIRONMENTS WITH EMPHASIS ON SOURCES AND FATE IN THE GREAT LAKES

R. J. Allan

6.1 INTRODUCTION

Much of the public concern over the use of organic pesticides and their environmental impact has arisen through the contamination of aquatic ecosystems by these toxic organic chemicals. One of the best examples of aquatic ecosystem contamination with organic pesticides has been the Great Lakes, where as early as the middle to late 1960s these chemicals were known to be present at levels which necessitated consumption guidelines for certain species of fish. Because of the shared responsibility of Canada and the United States for pollution prevention in the Great Lakes, the lakes have evolved as the world's most studied bodies of water with respect to organic pesticide sources, transport and fate (Allan *et al.*, 1991, 1991b). Recently, other parts of the developed world have begun to pay more serious attention to the contamination of freshwater by organic pesticides. However, in developing countries basic water quantity and quality issues still take precedence, although this does not mean that freshwater bodies in such countries are not threatened by contamination by organic pesticides and their residues, metabolites and impurities.

6.2 SOURCES OF ORGANIC PESTICIDES TO AQUATIC ECOSYSTEMS

Organic pesticides enter freshwater systems through a variety of sources, particularly via agricultural runoff (Fig. 6.1). In the Great Lakes, direct discharges or spills from manufacturing plants or other industries can also be serious sources. Another source is domestic and municipal uses of organic pesticides and their associated urban runoff. In the last decade, it has become increasingly clear that the atmosphere can be a major source of organic pesticides to the Great Lakes and thus for large lakes and reservoirs elsewhere. The origin of atmospherically-deposited organic pesticides may be far distant from the point of deposition. Organic pesticides may also be applied directly to aquatic ecosystems, for example to control black flies in western Canada or sea lamprey in the Great Lakes. Finally, specific industries can be sources of specific organic pesticides, for example chlorphenolic compounds used in the wood products industries.

On a global scale, agricultural uses remain the overall prime source of organic pesticides to aquatic ecosystems. With some of the exceptions referred to above, agricultural organic pesticides are applied to the soil or to vegetation followed by subsequent washoff and runoff to aquatic ecosystems. Some of these organic pesticides may also be wind-drifted into aquatic systems or may volatize and then be deposited by gaseous exchange, wet or dryfall at air/water interfaces.

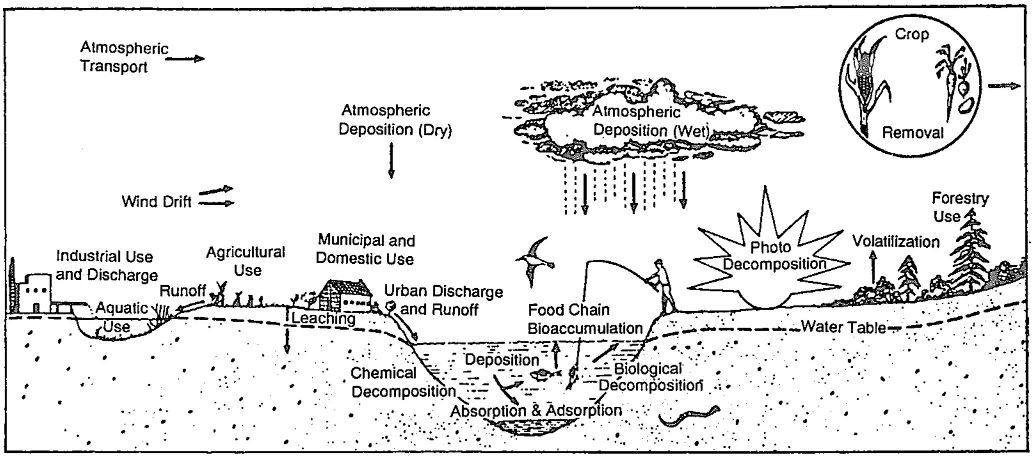


Fig.6.1 Pesticide uses and environmental pathways (after Gummer, 1980).

6.3 TYPES OF ORGANIC PESTICIDES AND THEIR USES

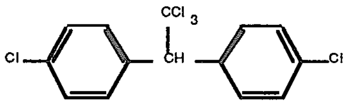
The chemicals discussed here are by definition toxic because they are used as pesticides and are intended to control or kill either plants or animals. Of the various organic pesticides used in agriculture, those which have resulted in the most serious long-term effects in freshwater ecosystems are not only highly toxic but also persistent and extensively used on a regional, national, continental or even global scale. In aquatic ecosystems, such chemicals can have deleterious effects on the biota exposed to them, to the wildlife which consume such biota, and even to the humans who consume either.

Three main types of organic pesticides have been or are widely used. The first group, the organochlorides (Table 6.1), is that dealt with here because they are toxic, persistent, bioaccumulate, and have been or are widely used. Typical structures of a few of the organochloride pesticides referred to in this text are given in Fig. 6.2. The second group of organic pesticides are the phosphorus containing pesticides and are usually insecticides. These phosphorus containing pesticides, however, are relatively immobile in comparison with the organochlorine pesticides, are rapidly degraded in the environment and seldom detectable in aquatic ecosystems except locally after application and immediate runoff. The organophosphorus pesticides thus do not generally fit the criteria of serious long-term, aquatic ecosystem contaminants. The third group, the carbamates are mainly insecticides and usually rapidly degraded after use, are relatively immobile, and seldom detected in aquatic ecosystems. Thus, the carbamates like the organophosphorus compounds, are also not considered long-term, serious aquatic ecosystem contaminants and are not discussed here.

Table 6.1 Main groups of chlorine containing organic pesticides and metabolites

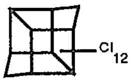
Group	Compound	Control uses
Organochlorine	aldrin	• insecticides
	dieldrin	- fleas
	endrin	
	α-BHC	- worms
	γ-BHC (lindane)	
	p,p'-DDD	- ticks
	p,p'-DDE	
	p,p'-DDT	- flies
	α -endosulfan	
	β -endosulfan	- bugs
	heptachlorepoxide	
	p,p' methoxychlor	- etc
Chlorophenoxyacids	2,4-D	• herbicides
	2,4-DB	- weeds
	2,4-DP	- broad leaf plants
	2,4,5-T	- etc.
	MCPA	

DDT



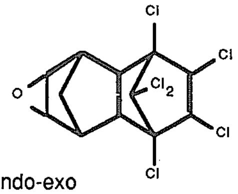
1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane

MIREX



dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta (*cd*) pentalene

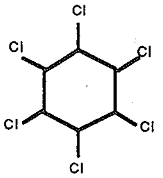
DIELDRIN



endo-exo

1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene

HCH (BHC)



1,2,3,4,5,6-hexachlorocyclohexane

Fig. 6.2 Four typical synthetic organic pesticides referred to frequently in the text.

The most serious organic pesticides in terms of impact on aquatic ecosystems were and are the chlorine-containing organo-chemicals. The prime reasons are their toxicity and the chemical properties which cause them to persist in the aquatic environment over long periods of time. This persistence results in their accumulation into food webs via bioconcentration and bioaccumulation to levels which can result in negative effects. The fate of organochlorine pesticides in aquatic ecosystems is of critical importance in terms of their eventual impact on biota including humans. The fate of organic pesticides is controlled by a series of factors (Table 6.2), many of them related to the chemical composition of the pesticide but also to the properties of the aquatic ecosystem itself, for example suspended particulate concentration or nutrient (trophic) status.

Table 6.2 Factors influencing the fate of organic pesticides

Physio-chemical	Biological	Other
solubility	bioaccumulation	runoff/precipitation
co-distillation	bioaccumulation	management practices
volatility	bio-uptake	wind-drift
photodegradation	bioavailability	erosion
stability		
temperature		
active life		
sorbtion		
formulation		

6.4 THE ROLE OF PARTICULATES IN THE TRANSPORT AND FATE OF ORGANIC PESTICIDES IN AQUATIC SYSTEMS

In aquatic ecosystems, the fate of persistent organic pesticides with a low (less than a few parts per million) solubility is highly dependent on sorption to particulates, the key process involved in their physical transport, degree of bioavailability, and thus eventual bioaccumulation and effects. Sorption and its controls in aquatic ecosystems are thus discussed here in some detail because it is perhaps the most critical factor in the fate and thus effects of persistent organic pesticides.

Because particulates reduce the organic pesticide concentration in solution, they buffer the immediately and directly bioavailable aqueous phase contaminant concentration. Concentration of competing organic pesticides in water, suspended solids type, and a host of other factors preclude a simple systematic procedure for predicting sorption characteristics of these chemicals to aquatic sediments. Nevertheless, given a specific concentration of an organic pesticide in water and a measured partition coefficient (Kow) a prediction can be made of the expected concentration to be associated with the particulate phase (Fig. 6.3). The Kow is measured as an equilibrium constant between the concentration of contaminant in the particulate phase and the concentration in solution at a given sediment concentration.

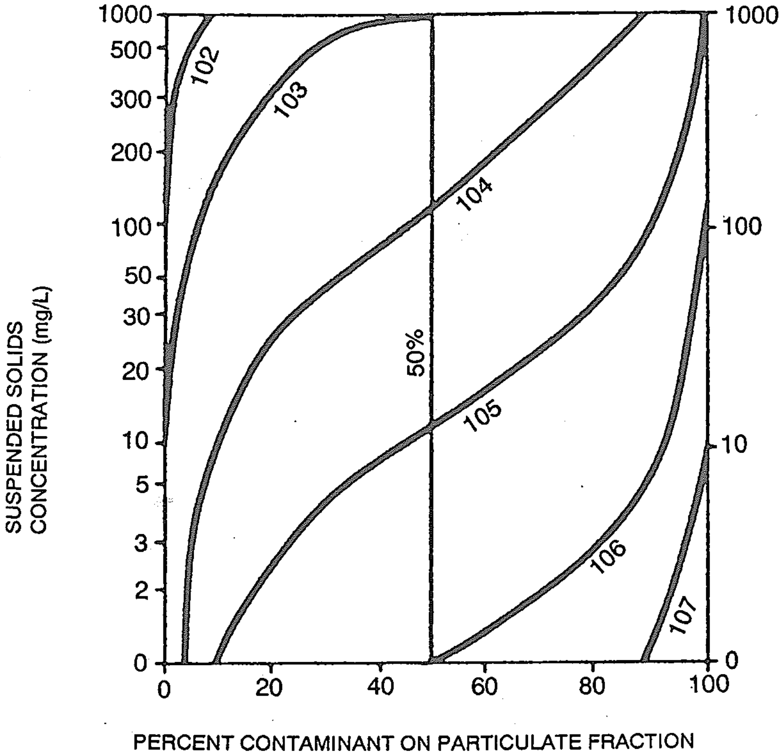


Fig. 6.3 Relationship between concentration of suspended particulates in aquatic ecosystems and the percent of organic pesticides with different Kow's transported in the suspended particulate phase.

In natural aquatic ecosystems, the first and most important characteristic affecting Kow is the concentration of the chemical in solution. This concentration of the organic pesticide in solution thus controls the amount sorbed but only at relatively low sediment concentrations of up to 20 mg/L.

Second and third controlling factors are particulate concentration and type. Connor and Connolly (1980) showed an inverse relationship between concentration of absorbing solids and partition coefficient (the ratio of the solid phase concentration to the dissolved phase concentration in the linear portion of the Langmuir sorption isotherm) (Fig. 6.4). A change in a specific sediment concentration from 100 mg/L to 1000 mg/L lowered the partition coefficient for Kepone from 5900 to 3400 (Fig. 6.4). Above sediment concentration of 20mg/L, the sorption relationship was no longer linear and progressively less of the pesticide became absorbed or the Kow decreased. Particulate type also caused differences in DDT sorption, for example on illite versus montmorillonite and of Kepone soprtion on James River sediment versus Range Point Marsh sediment (Fig. 6.4).

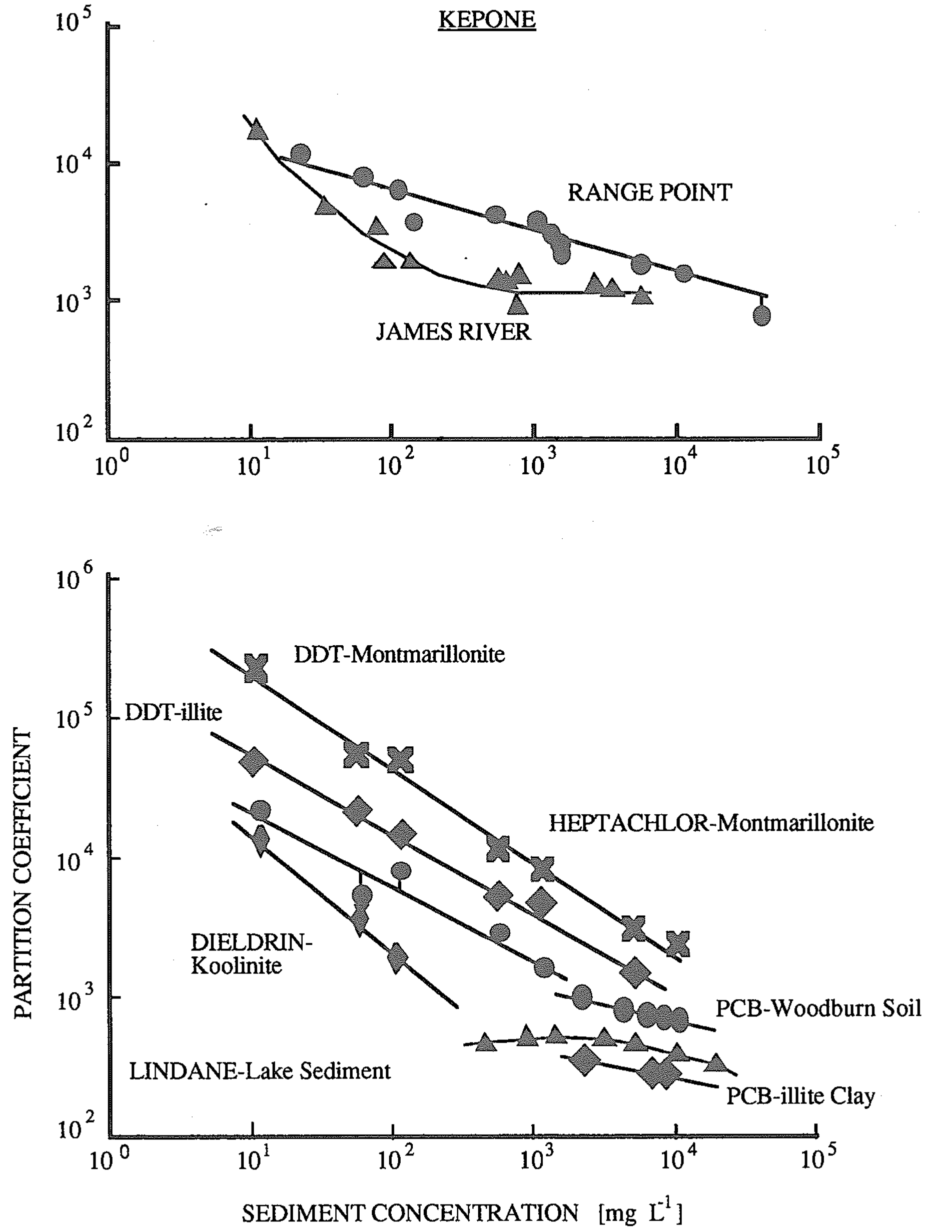


Fig. 6.4 Partition coefficient as a function of the concentration of particulates and particulate type (after Connor and Connolly, 1980).

The fourth important particulate parameter controlling organic pesticide partitioning is natural organic content of the particulates. Suspended particulates in aquatic systems can be entirely organic, namely zooplankton, phytoplankton and bacteria or their excretions. Centrifugation of this material in lakes usually produces a dark, organic, rich paste, which by virtue of sorption and bioaccumulation may contain very high concentrations of organic pesticides. Other suspended particulates, especially resuspended bottom sediments in the Great Lakes, are made up primarily of inorganic materials, and usually have an organic carbon content of some 3%. When such relatively low percentages of organic matter are present, most of this may be in the form of thin coatings on mineral substrates. In fact, removal of organic pesticides from solution and their partitioning onto particulates may not be so much of a sorption process as one of exclusion and solubilization of the organic pesticide into (or onto) an organic (lipid-like) surface layer coating inorganic particulates.

Lastly, time affects sorption of organic pesticides in that some 60% of total sorption is usually complete in two to five minutes. Equilibrium is established extremely rapidly in relation to the time required for aquatic ecosystem, contamination and/or eventual media sampling. There are thus two components to the sorption of organic pesticides: (1) a rapid component completed in a very short time period; and (2) a slower component that often occurs after a period of minutes or hours but can continue for weeks, months, or longer. Conventional Kow's determined in laboratories are usually a measure of only the rapid component. However, in natural aquatic ecosystems where exposure times can be for years, the lower sorption component may become important. Alternatively, when organic pesticides are desorbed, it is usually only the rapid component that becomes readily bioavailable. The slower component may also eventually become bioavailable in natural aquatic ecosystems. Pavlou and Dester (1980) summarized partition coefficients for classes of organic pesticides that occur in aquatic ecosystems. The range for high to low Kow follows a shift from non-polar to polar characteristics, which primarily results in changes in water solubility (Table 6.3).

Table 6.3 Estimated Range of Sediment/Water Partition Coefficients for Various Pesticide Classes (after Pavlou and Dexter, 1980).

Pesticide type	Kow	Characteristics of adsorption (sediments)
Organochlorines		
Aromatic	10^5-10^3	Few polar moieties; hydrophobic and van der Waals interactions; induction effects (polar substituents, non-conjugated double bonds).
Aliphatic		
Organophosphates		
Aliphatic derivatives	$5x10^2$-10^1	Active polar moieties (electron-rich heteroatoms, acid hydrogens, heterocyclic nitrogen).
Phenyl derivatives	10^3-10^2,	
Heterocyclic	$5x10^2$-50	
Carbamates		
Methyl carbamates	$5x10^2$-2	Highly polar; enhanced solubility; reduced adsorption vs. organochlorines
Thiocarbamates	$5x10^2$-50	
Triazines	8-1	Solar ionizable groups (amino-hydrogens); hydrogen bonding with water; low adsorption on soils.

Predicting the actual fate of pesticides associated with fine-grained particulates is far more difficult than when the organic pesticides are in solution because the dynamics of small particles are governed by a host of physical, chemical and biological processes. Once an organic pesticide has become associated with a particulate, its fate is influenced by many processes including:

(i) Sorption/desorption
(ii) Flocculation
(iii) Precipitation and co-precipitation
(iv) Degradation and transformations
(v) Bioaccumulation
(vi) Short-term events (floods, high wind stress)
(vii) Sedimentation rates
(viii) Resuspension episodes
(ix) Mixing
(x) Pore water release
(xi) Mineralization
(xii) Burial.

6.5 ORGANIC PESTICIDE TRANSPORT AND FATE IN THE GREAT LAKES

Evidence of pollution of waterways by organic pesticides is not as readily available as might be expected. The database on the Great Lakes and its basin is probably the most extensive as far as lakes are concerned. In the ILEC Book of World Lakes (ILEC, 1988 and 1989), data for organic pesticides is rare and usually on DDT or related chemicals in fish. For world rivers, one of the most extensive data sets is perhaps on the Mississippi River system (Pereira *et al.*, 1990). Pesticide information on this river and some other major world rivers can be found in a Special Volume of Science of the Total Environment on the Fate and Effects of Toxic Chemicals in Large Rivers and Their Estuaries (Allan *et al.*, 1990).

6.5.1 Tributary Inputs of Organic Pesticides to the Great Lakes

Suspended particulates from the mouths of 105 Canadian streams flowing into Lakes Ontario, Erie and Huron (Frank *et al.*, 1981a) were contaminated with DDT and its metabolites. The highest mean concentration of total DDT was 365 ppb for streams draining to Lake Ontario from the Niagara Peninsula. The highest suspended particulate loadings of DDT were in streams with the greatest suspended sediment loads. Of the main organic pesticides analyzed, DDT and dieldrin were detected most frequently. From the concentrations of organic pesticides in the 105 streams and the total annual suspended particulate loads of the streams, the total particulate loads of various organic pesticides to various sections of the lower Great Lakes could be calculated (Table 6.4).

Similar river mouth investigations were made to determine the quantities of Triazine residues carried to the Great Lakes by rivers in Canada (Frank *et al.*, 1979 and 1981a). The highest mean concentrations of Triazine residues (4 µg/L) occurred in stream water entering Lake Erie. Triazine has a low Kow and residues were not detected in suspended particulates. Concentrations of various pesticides, including DDT, dieldrin, chlordane and Triazine were determined in the Grand River (Table 6.5), which has the largest drainage basin on the Canadian side of the Great Lakes (Frank *et al.*, 1981a). Only persistent organic pesticides were detected at the river mouth, although many known non-persistent organic pesticides were also detected near sites of application shortly after use. Triazine was the most widely used pesticide, but only 0.6% of that applied reached the mouth of the Grand River.

Table 6.4 Crude loadings calculated from concentrations of pesticides in suspended particulates and mean annual discharges (after Frank et al., 1981a).

Lakes and lake sections		No. of streams	Suspended solids loadings (metric tons/yr)	Crude loadings (g)	
				ΣDDT	Dieldrin
Bay of Quinte,	Lake Ontario	7	50,676	991	19.2
North Shore,	Lake Ontario	23	89,529	1,458	135
Southwest Shore,	Lake Ontario	12	8,352	1,002	26.7
Niagara River	tributaries	5	1,406	72.9	0.57
North Shore,	Lake Erie	18	154,135	6,866	240
Detroit River	tributaries	3	12,047	427	51.6

Table 6.5 Concentrations of persistent organic pesticides in bottom sediments, suspended particulates and whole water at the mouth of the Grand River, Ontario (after Frank, 1981 and Frank et al., 1981a).

		River Bed Sediments⁽¹⁾ (µg/kg) [ppb])		Suspended Sediments (µg/kg [ppb])		Whole Water (ng/L [ppt])	
Year	Chemicals	Mean	Range	Mean	Range	Mean	Range
1975-76	ΣDDT	10	5-15	2.7	ND-24		
	Chlordane (AS BELOW)	2	1-3	0.4	ND-5		
	Dieldrin	0.9	ND-1.9	0.7	ND-4		
	Heptachlor epoxide	4.77	ND-9.4	0.07	ND-1		
1976-77	ΣDDT	21	ND-60	13	ND-65	1.5	ND-15
	α-BHC	3	ND-10	2	ND-10	ND	ND
	Chlordane	6	ND-17	4.5	ND-3	0.1	ND-1
	Dieldrin	2	ND-5	0.3	ND-3	0.4	ND-2
	Endrin	1	ND-2	ND	ND	0.1	ND-1
	Heptachlor epoxide	1	ND-3	0.3	ND-3	0.03	ND-1

(1) Values for bottom sediment determined only once.
ND = not detected.

6.5.2 The Atmosphere as a Source of Organic Pesticides to the Great Lakes

Many of the most toxic chlorinated pesticides have been input directly to the Great Lakes from point and non-point land-based sources. However, it has become increasingly clear in the last few years that a major source for many chlorinated organic pesticides to these large lakes is by deposition from the atmosphere. Several of the same chemicals, α-BHC, dieldrin, lindane and DDT occur in wet precipitation in many parts of Canada and the world. In rain from across Canada, the overall mean annual concentration for α-BHC, dieldrin, lindane and p,p'-DDE were 21 ppt for α-BHD and lindane; 0.29 ppt for dieldrin; and 0.09 ppt for p,p'-DDE (Strachan, 1988). Concentrations of these organic pesticides in rain samples were similar from across southern Canada and from around the Canadian side of the Great Lakes. The total organic pesticide load to each Great Lake thus depends more on the quantity of rainfall and the surface area of the lake than on the variation in organic pesticide concentration in the actual rain.

To estimate the atmospheric input of organic pesticides to the Great Lakes, Strachan and Eisenreich (1987) attempted to determine mass balances. Although the Great Lakes have possibly more total data on organic pesticide concentrations in various lake media than any other lakes of the world, the data base was extremely poor when the requirement was to close a mass balance. Point source and tributary inputs were usually unquantified as were non-point source inputs from runoff, combined sewers, or from groundwater. Accurate water analyses to obtain real "dissolved" concentrations were, and are, rare and the use of non-detected concentrations to calculate mean loads becomes questionable. DDT was the only organic pesticide for which mass balances could eventually be completed with some confidence. The atmospheric load of total DDT to Lakes Superior, Michigan, Huron, Erie and Ontario were calculated as 90, 64, 65, 33 and 26 kg/yr respectively, and translated to 97, 98, 97, 22 and 31% of the total DDT loads to the respective lakes (Fig. 6.5).

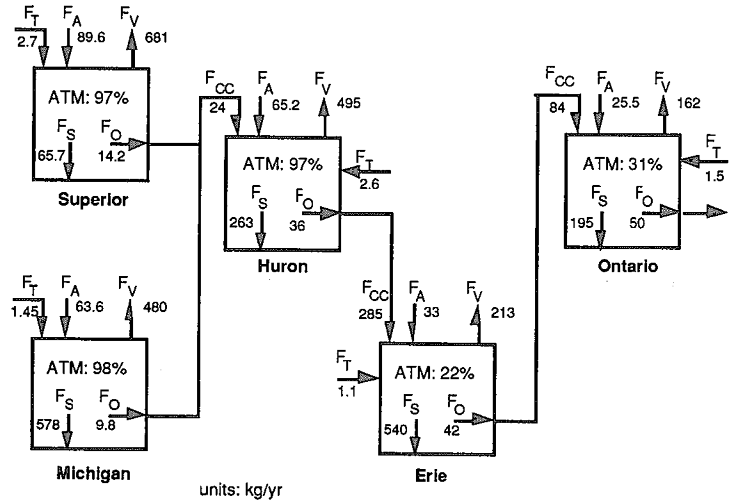


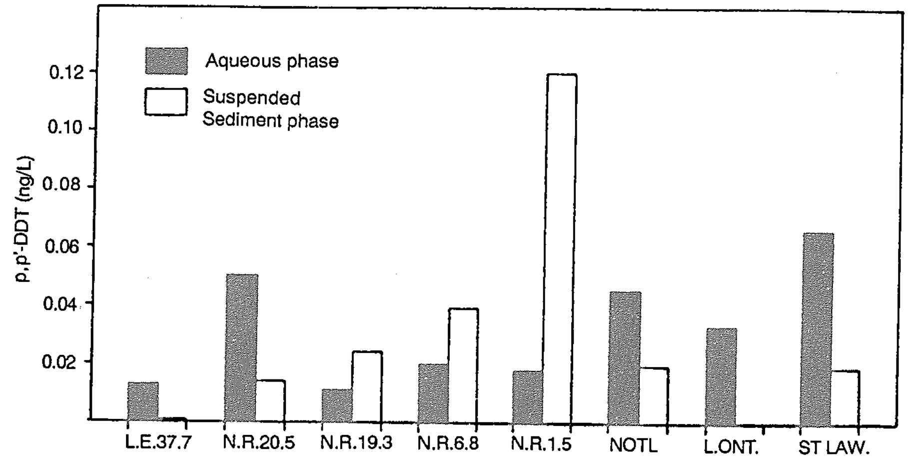
Fig. 6.5 Great Lakes mass balance model: total-DDT (F=Flux; T=Tributaries; A=Atmosphere; V=volatilization; s=sediments; o=out-flows; cc=connecting channels (rivers).

6.5.3 Partitioning of Organic Pesticides in the Great Lakes/St. Lawrence River System

Canadian studies of organic pesticide transport and fate in aquatic ecosystems began seriously around 1980 with the investigation of the loads of such chemicals from the Niagara River to Lake Ontario. These studies required the development of large volume water extractors (McCrea and Fischer, 1985) which allowed detection of extremely low (ppt and ppq) concentrations of organic pesticides in the "dissolved" phase. This operationally defined "dissolved" phase was the content of the elutriate from a high speed centrifuge. The material collected by the centrifuge was considered the "particulate" phase.

The concentration of organic pesticides in the Niagara River were extremely low (in the ppt range), but their total load transported into Lake Ontario is considerable given the large flow of some 6,000 m^3/sec. The distributions of p,p'-DDT and BHC in the operationally defined "aqueous and particulate" phases of the river (McCrea *et al.*, 1985) are shown in Fig. 6.6. Organic pesticides such as lindane (γ-BHC) with low partitioning coefficients (Kow's) were transported primarily in the "dissolved" phase (Fig. 6.6). Although organic pesticides with high sediment-partitioning coefficients such as p,p'-DDT were concentrated in the suspended solids phase (Fig. 6.6), much of the load of these pesticides was still transported in the operationally defined "dissolved" phase because of the low suspended particulate concentrations in the Niagara River (1 to 10 mg/L).

More recent research on organic pesticide fate has been conducted on the St. Lawrence River which drains the Great Lakes to the Atlantic Ocean. At its source in Lake Ontario, the flow of the St. Lawrence River is some 7,700 m^3/sec., and at its mouth near Quebec City, some 12,000 m^3/sec. A given water mass traverses the river in five to seven days. Concentrations of suspended solids in the river vary from some 1 mg/L at the river's source to some 10 mg/L at the upper end of the St. Lawrence estuary. Whole water samples collected along the St. Lawrence River from its source to estuary were processed by high speed centrifuge and large volume water extraction of the effluent. A comparison of the changes in the fraction of the organic pesticide loads transported in the operationally defined particulate versus dissolved phases showed that total DDT, BHC and dieldrin concentrations in the suspended solids decreased downstream (Fig. 6.7) (Kaiser *et al.*, 1990). However, the progressive downstream increase in suspended particulate load meant that the load of these pesticides transported by the river remained relatively constant.



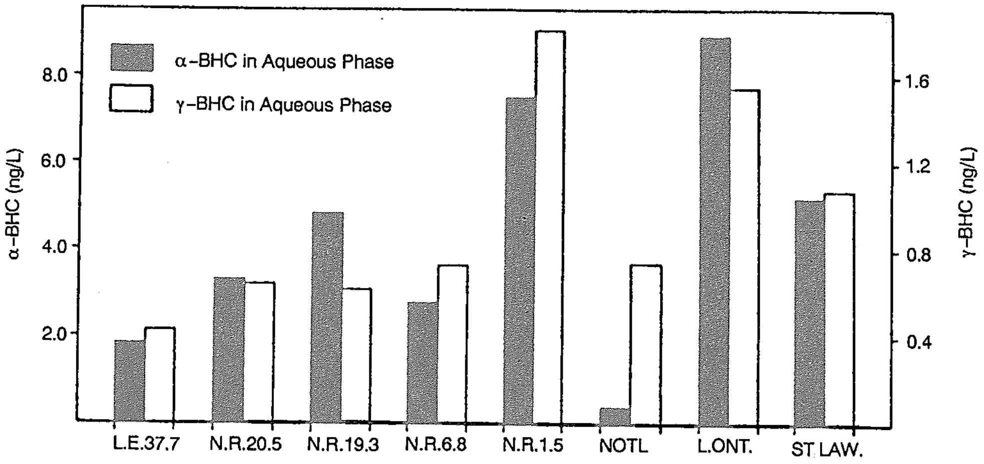


Fig. 6.6 p,p'-DDT and BHC distribution in the aqueous and suspended sediments phase of the Niagara River (LE=Lake Erie; NR=Niagara River; NOTL=Niagara-on-the-Lake; L.ONT=Lake Ontario; ST.LAW=St. Lawrence River).

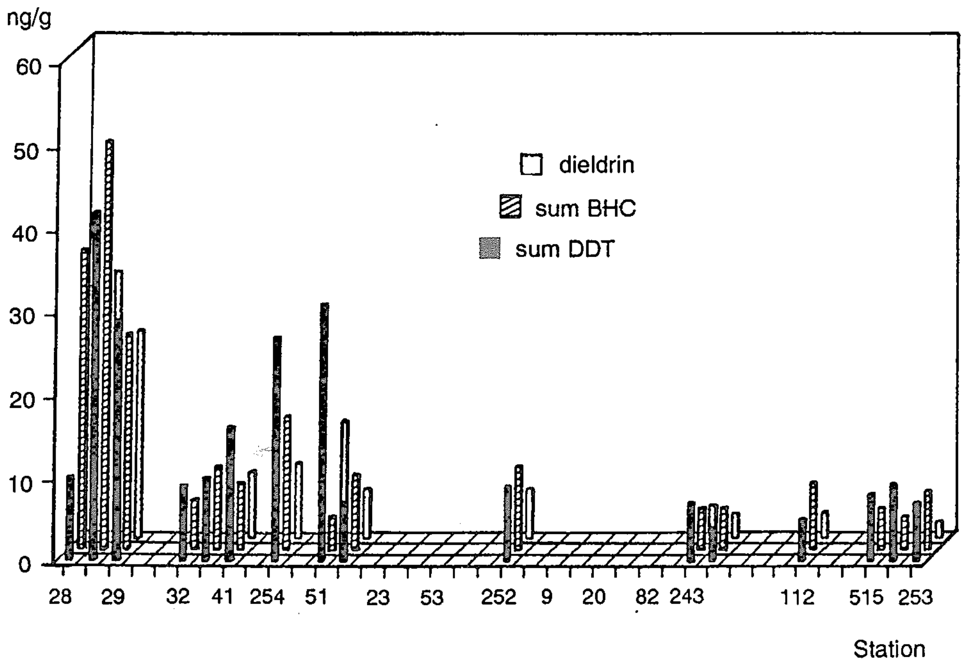


Fig. 6.7 Concentrations of total BHC, dieldrin and total DDT in St. Lawrence River suspended sediments in 1987 (after Kaiser *et al.*, 1990). (Station 28/29 is at the source of the river at Lake Ontario, and stations 515 and 253 are near the mouth of the river.)

6.5.4 Lake Bottom Sediments as a Sink and Source of Toxic Organic Pesticides in the Great Lakes

Most of the persistent organic pesticides introduced into the Great Lakes are hydrophobic and partition onto suspended particulates. A major aspect of the fate of these organic pesticides, for example DDT in Lake Michigan, is thus to settle on the lake bottom and become redistributed by currents to areas of sediment focusing (Fig. 6.8). At such sites, organic pesticides and their metabolites are eventually buried by new layers of less contaminated sediments. The distribution of Mirex in a sediment core from Lake Ontario is a typical example of this burial and natural decontamination process (Fig. 6.9). However, although lake bottom sediments are eventually a final sink for persistent organic pesticides, there is an intermediate stage during which physical, biological and chemical limnological processes may recycle these pesticides back into the water column and food web.

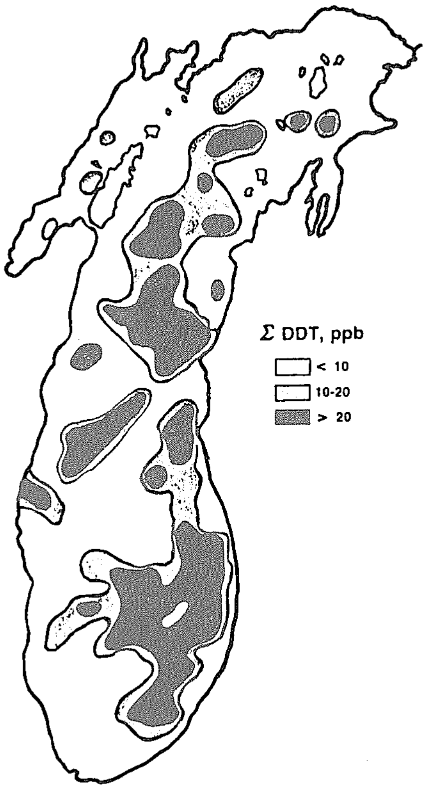


Fig. 6.8 Distribution of total DDT in surficial bottom sediments of Lake Michigan (0-3 cm) (after Frank *et al.*, 1981a).

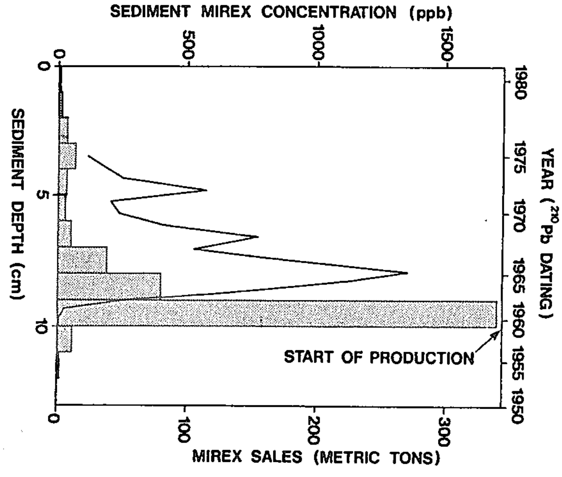


Fig. 6.9 Distribution of Mirex in a sediment core from western Lake Ontario (Durham and Oliver, 1983). Bars are concentrations; single line is sales.

6.5.5 Long Range Aquatic Transport of Organic Pesticides

The insecticide Mirex was first discovered at the eastern end of Lake Ontario in 1974 (Kaiser, 1974). It was, and is, a classic example of an industrial point source input of an organic pesticide to a major aquatic ecosystem. The two point sources were on the Niagara and Oswego Rivers draining to Lake Ontario. In the late 1980s, new sampling and analytical techniques revealed that Mirex had been transported in the water column to the St. Lawrence estuary. The concentration of Mirex in suspended particulates declined downstream in the St. Lawrence River from its source in Lake Ontario to the estuary. The concentrations of Mirex in suspended particulates at the source of the St. Lawrence are around 5 ppb and decreased to 1 ppb near Quebec City (Fig. 6.10). These concentrations translate to a flux of some 1 to 2 kg of Mirex/year. Mirex could also be detected in the operationally "dissolved" phase and the highest concentration was 13 pp quadrillion (Kaiser *et al.*, 1990). Nevertheless, the insecticide was still detectable some 600 to 1,000 km respectively downstream from the two sites of its original introduction. The dispersal of this highly hydrophobic organic insecticide throughout the Niagara River - Lake Ontario - St. Lawrence River system, a distance of over 1,000 km, is clear evidence of the potential long-range aquatic dispersion of persistent organic pesticides on a scale which only now can be quantified by analyses of abiotic water column media.

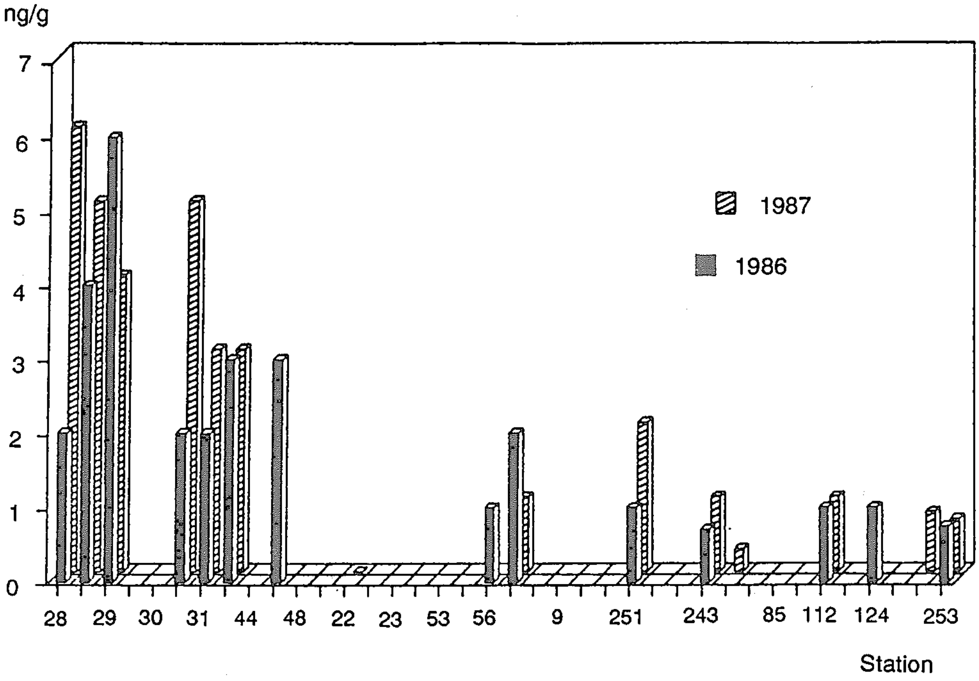


Fig. 6.10 Mirex concentrations (ng g^{-1} dry wt) in suspended sediments of the St. Lawrence River, 1986 and 1987. (See Figure 6.7 for key to station locations.)

6.5.6 Bioaccumulation of Organic Pesticides in the North American Great Lakes: The DDT and Mirex Case Studies

The preferred sample media to detect organic pesticides in the Great Lakes have been biological, namely predator fish and the eggs of fish-eating herring gulls. In these biotic media, organic pesticide concentrations are in the ppm and high ppb range. Even so, much of the published data has only appeared since 1980 and especially over the last five years (Tables 6.6, 6.7 and 6.8). Concentration trends for chlorinated organic pesticides in most predatory fish from the Great Lakes have shown dramatic declines relative to concentrations ten and twenty years ago. The concentrations of some organic pesticides such as DDT were extremely high in lake trout in the early seventies, particularly in Lakes Michigan and Ontario (Fig. 6. 11). The highest DDT concentrations in lake trout from Lake Ontario were around 4.5 ppm in 1977 and by 1985 these concentrations were reduced to about 1 ppm. Concentrations of DDT in lake trout in lakes Superior, Erie and even Ontario were much less than in Lake Michigan where lake trout in 1970 were recorded as containing some 19 ppm DDT. Declining Mirex concentrations can be detected in spottail shiners from the Niagara River (Fig. 6.12). The eggs of the fish-eating herring gull show similar downward trends in concentrations of organic pesticides, including the DDT metabolite DDE (Fig. 6.13).

Table 6.6 Comparative mean values for organochlorine insecticides in Lake Ontario and Lake Erie biota (ng/g [ppb] dry weight) (after Whittle and Fitzsimons, 1983).

Sample medium and site	% Lipid	ΣDDT	Mirex
Surface netplankton			
Western Basin, Lake Ontario	16.0	72	ND
Eastern Basin, Lake Ontario	13.3	63	ND
Mysis			
Western Basin, Lake Ontario	7.9	59	ND
Eastern Basin, Lake Ontario	3.9	79	ND
Smelt			
Western Basin, Lake Ontario	5.6	533	35
Eastern Basin, Lake Ontario	4.4	390	50
Eastern Basin, Lake Erie	4.1	141	ND

ND=not detected

Table 6.7 Mean size and total DDT concentrations (dry weight basis) for organisms from the eastern and western basins of Lake Ontario (ppb [ng/g])* (after Borgmann and Whittle, 1983).

Organism	Body weight (g)	Total DDT E. Basin	W. Basin
Zooplankton	2×10^{-6}	60	80
Amphipods	1.3×10^{-3}	690	480
Mysids	5.3×10^{-3}	120	280
Sculpins	0.66	970	---
Smelt	4.2	780	2200
Lake trout	246	4920	5700
Coho salmon	434	---	3260

*Number of samples: 20 and 4 for zooplankton; 8 and 4 for amphipods; 12 and 41 for mysids, and over 50 for all three fish in the Eastern and Western basins respectively.

Table 6.8 Mirex concentrations in Lake Ontario fish (standard fillet sample) (after Armstrong and Sloan, 1980).

Species	Origin	Total Mirex (ppm) 1976	 1977	 1978
Rainbow trout	Lake	0.05	0.17	--
Brown trout	Lake	0.09	0.16	0.11
Lake trout	Lake	0.22	0.24	0.35
White perch	West of Oswego River*	0.11	0.16	0.14
White perch	Oswego River and east	0.04	0.14	0.13
Smallmouth bass	West of Oswego River	0.12	0.36	--
Smallmouth bass	Oswego River and east	0.10	0.29	--

*The Oswego River was the second major source of Mirex to Lake Ontario, after the Niagara River.

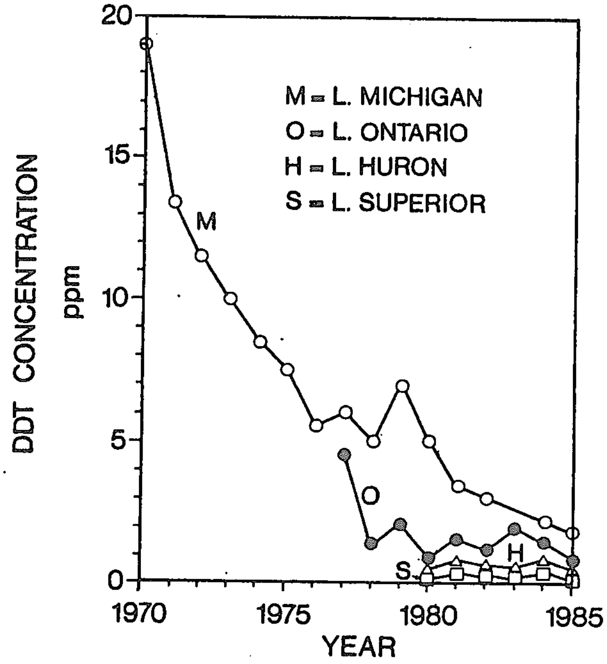


Fig. 6.11 DDT concentration trends in lake trout in the Great Lakes (adapted from IJC, 1987).

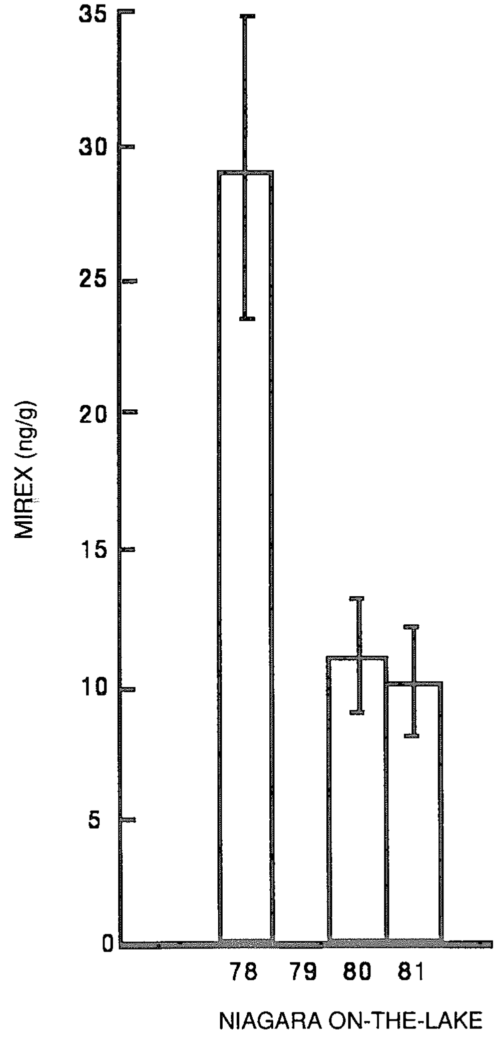


Fig. 6.12 Mean Mirex residues (with 95% confidence limits) in young-of- the-year spottail shiners from the Niagara River (after Suns et al., 1981).

In 1983, concentration trends for some persistent organic pesticides in Lake Ontario lake trout indicated a leveling out or even an increase in 1982 and 1983. More recent data seem to continue the downward trend. Fluctuations in concentrations may now have as much to do with internal limnological processes such as frequency of storms and related contaminated bottom sediment resuspension or annual events of hypolimnetic upwelling, as with the actual load of persistent organic pesticides still entering the lakes even from the atmosphere. Organic pesticide concentrations in herring gull eggs for 1989 are given in Table 6.9.

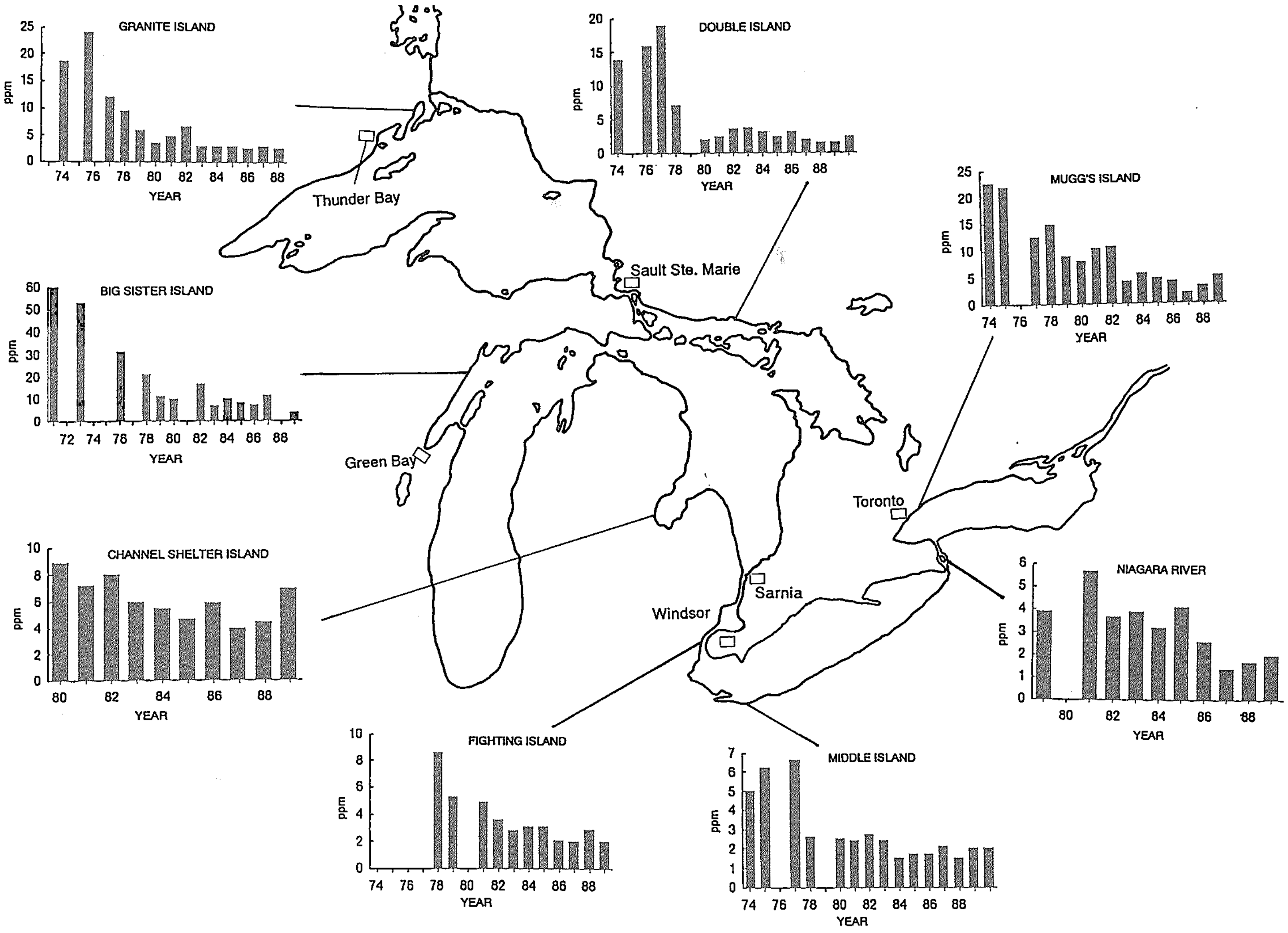


Figure 6.13 Trends in DDE Concentrations in Great Lakes Herring Gull Eggs (after Allan *et al.*, 1991).

Table 6.9 DDE and Mirex Concentrations in Herring Gull Eggs(1) from Colonies on the Great Lakes, 1989.

	DDE	Mirex
	----------ppm----------	
Lake Ontario	5.25	1.15
Lake Erie	2.70	0.12
Lake Huron	3.39	0.09
Lake Superior	2.50	0.07
Lake Michigan	4.85	0.03

(1) Data are mean values based on individual analyses of a 10 egg pool for each colony sampled.

The bioaccumulation of organic pesticides in biota of the Great Lakes is well documented. However, concentrations in water are often given in ppt or ppq, whereas those in sediments and biota are in ppb and ppm. This can lead to a misconception of the degree of bioaccumulation. Concentrations of organic pesticides in the abiotic and biotic compartments of Lake Ontario are all presented in ppt (ng/kg) in Table 6.10, which gives a better comparison of their degree of bioaccumulation in contaminated aquatic ecosystems.

Water concentrations of organic pesticides in the Great Lakes are within the guidelines (Table 6.11) developed for the Great Lakes by the Canada-United States International Joint Commission, although bioaccumulation of these same organic pesticides has led to the need for fish consumption guidelines (Table 6.12).

Table 6.10 Summary and range of concentrations of organic pesticides in Lake Ontario media (ppt or ng/kg [L])* (Compiled from Borgmann and Whittle, 1983; Fox *et al.*, 1983; Strachan and Edwards, 1984; Weseloh, 1983).

	Total DDT	Mirex	Lindane
Raw water	0.3-57	0.1	0.4-11
Bottom sediment	25,000-218,000	144,000	46,000
Benthos	440,000-1,088,000	41,000-228,000	NA
"Suspended" sediments	40,000	15,000	1,000-12,000
Plankton	63,000-72,000	ND-12,000	12,000
Fishes	620,000-7,700,000	50,000-340,000	2,000-360,000
Herring gull eggs	7,700,000- -34,000,000	1,800,000- -6,350,000	78,000

*These values are only of the crudest nature and are not statistical means. Where only one value is given, the numbers are means, often of widely ranging values. Where a range is given, several sources of data were involved. ND=not detected; NA=not analyzed.

Table 6.11 Objectives for persistent organic pesticides in Lake Ontario.

Chemical	Concentration in Lake Ontario water	IJC (water quality objectives) (1)	Drinking water guidelines Canada	WHO
	ppt			
DDT (total)	0.12 (1986 median, n-14)	3	30,000	1,000,000
Dieldrin	0.33 (1986 mean, n-31)	1(2)	700	30
Lindane	1.3 (1986 mean, n-31)	10	---	4,000
Toxaphene	ND(3) (1983, n-14)	8	5,000	---
Mirex	ND	DL(4)	---	---

(1) The IJC (Canada-United States International Joint Commission) Objectives are for the protection of the most sensitive aquatic life.

(2) Aldrin/dieldrin total.

(3) Not detected.

(4) Detection limit presently 5 ppt.

Table 6.12 Fish consumption criteria(1)

	Great Lakes Agreement Objectives(2)	Canada Health & Welfare Regulatory Limit(3)	US FDA Action Level(4)	Ontario Sport Consumption Guidelines(5)
	(parts per million, wet weight)			
Aldrin/Dieldrin	0.3	0.1	0.3	--
DDT (total)	1.0(6)	5.0	5.0	5.0
Endrin	0.3	0.1	0.3	--
Heptachlor (total)	0.3	0.1	0.3	--
Lindane	0.3	0.1	0.3	--
Mirex	substantially absent	0.1	0.1	0.1(6)
Toxaphene	--	0.1	5.0	--

(1) Criteria based on skinless fillet unless otherwise footnoted.

(2) Based on the protection of the most sensitive species, which accounts for lower values for some compounds.

(3) Applies to fish in commerce only. The Province of Ontario applies these guidelines to sport fish consumption.

(4) US Food and Drug Administration (FDA) action levels based on fillet with skin on.

(5) Ontario guidelines refer to restricted frequency of consumption of fish: if level of a single contaminant in a skinless dorsal fillet is below the guidelines then unrestricted consumption is allowed; if the level exceeds the guideline then restriction in frequency of fish meals is advised. For women of child-bearing age and children under 15 years, restrictions apply below the guideline levels and no consumption is recommended for levels that exceed the guidelines.

(6) Criteria based on whole fish.

6.6 GLOBAL USE OF PESTICIDES AND THEIR POTENTIAL IMPACT

Organic pesticides are used around the world. The production of synthetic organic pesticides accelerated during and after World War 2 with the discovery and development of DDT and chlorinated phenoxy herbicides. Over the next forty years, from 1950 to 1990, production and global use of organic pesticides has increased dramatically. The first generation of pesticides were simple stomach poisons and mainly contained arsenic or other heavy metals and metalloids. The next generation of pesticides were the organochlorines, organophosphates and carbamates. The future generation will be the biorationals, chemicals produced naturally by plants and animals and ones that do not necessarily kill.

The world market for pesticides is at some 16 billion United States dollars. The U.S.A. use represents some 25% of this total. In 1987, U.S.A. manufacturers produced some 1.4 billion pounds in synthetic organic pesticides valued at some US$4.4 billion. The agricultural share of pesticide use in the U.S.A. is some 75% of total users. Outside the U.S.A., the rest of the world uses organic pesticides at an ever-increasing rate as more countries become agriculturally developed.

The global contamination of waterways by pesticides may be approached in a very general way by looking at the national use of pesticides (Table 6.13). As might be expected, the large agriculturally developed countries are the major users, i.e. the U.S.A., U.S.S.R., China and Australia. Other major users are small, highly-mechanized, intensively farmed countries such as France, Italy, Spain and Japan. Large developing nations such as Brazil and India also fall into the top ten users. The foci of use appear to be the United States and Europe west of the Urals. The use of pesticides in the northern hemisphere may be ten times that in the southern hemisphere (Table 6.13) and this could be reflected in the general hemispheric atmospheric concentrations of pesticides and thus eventual input to and concentrations in remote aquatic ecosystems.

6.7 CONCLUSIONS

Large amounts of organic pesticides are used around the world. In some developed countries, the intensity of usage is high because of their small area under agricultural production. The amounts used in the northern hemisphere far outweigh those used in the southern hemisphere. The main foci of use in the northern hemisphere are the United States, Europe west of the Urals, and the Far East. In North America, a major database on concentrations and fate of pesticides in aquatic ecosystems is in the Great Lakes. In these lakes, in spite of their dimensions, organic pesticides are found in all compartments. Highest concentrations are associated either with bottom lake sediments or with predator fish. Due to bioaccumulation of persistent organic pesticides, very high concentrations of specific organic pesticides have been recorded in a variety of biota. Because of this, human consumption guidelines for certain fish have been developed.

The concentrations of most organic pesticides in sediments and biota of the Great Lakes have declined, often dramatically, over the last twenty-five years. Nevertheless, for some organochlorine pesticides, these declines have levelled off. Part of the reason is that the atmosphere has become a major source of some organochlorine pesticides now that more traditional point and non-point sources have been controlled.

The case studies of pesticide distribution and bioaccumulation in the Great Lakes are based on an extensive database. They imply that similar aquatic ecosystem contamination is likely to have occurred in other agricultural areas and in the vicinity of major organic pesticide production facilities. Also, recent mass balance calculations of organochlorine pesticide sources to the Great Lakes imply that the atmosphere is now a major course of these chemicals to large bodies of water and will thus be the major source of the same pesticides to remote lakes and reservoirs outside the main industrial and agricultural zones of the world. Given use of organic pesticides in the northern versus the southern hemisphere, the problem of atmospheric inputs of organic pesticides to remote aquatic ecosystems may be grater in the former. However, the types of organic pesticides used in developing versus developed countries tend to be the older, more toxic and more persistent organochlorine pesticides.

A global programme to assess the state of contamination of major lakes, rivers, and estuaries by formerly and presently used organic pesticides needs to be undertaken. In addition, a global procedure to assess historical trends of atmospheric organic pesticide input to major lakes and reservoirs in remote areas should be undertaken by analysis of radiodated lake bottom sediment cores.

Table 6.13 Global use of pesticides (extracted from World Resources, 1990-91)(1)

CONTINENTAL ZONE/ COUNTRY/ HEMISPHERE	ANNUAL AVERAGE USE	
	1975-77	1982-84
	10^3 tonnes active ingredient	
North America	545	498
South America	113	104
Africa	76	66
Asia	293	324
Soviet Union	349	535
Europe	511	588
Australia	64	68
Soviet Union(2)	349	535
United States	459	373
China	150	159
France	83	99
Italy	84	98
Spain	55	72
Australia	61	65
India	53	53
Brazil	59	47
Japan	34	32
Northern Hemisphere	1,760	2,006
Southern Hemisphere	199	185

(1) To nearest 103 tonnes. Does not 'balance' efficacy (toxicity) of active ingredient, e.g. 1 tonne pyrethroid may equal 10-30 tonnes of DDT. Land area is important in terms of intensity of use in each country, but comparisons between continents may give a better estimate of the distribution of global use. Countries which provide no data are not major users.
(2) Top ten global users in 1982-84.

REFERENCES

Allan, R.J. 1986. The role of particulate matter in the fate of contaminants in aquatic ecosystems. Inland Waters Directorate Scientific Series No. 142, 128 pp.

Allan, R.J., Campbell, P.G.C., Förstner, U., and K.R. Lum (*Eds.*). 1990. The Fate and Effects of Toxic Chemicals in Large Rivers and Their Estuaries. Science of the Total Environment 97/98, 871 pp.

Allan, R.J., Ball, A.J., Cairns, V., Fox, G.A., Gilman, A.P., Peakall, D.B., Piekarz, D., Van Oostdam, J.C., Villeneuve, D.C. and D.C. Williams. 1991a. Toxic Chemicals in the Great Lakes and Associated Effects. Volume I. Contaminant levels and trends. Pub. Govt. of Canada, 420 pp.

Allan, R.J., Ball, A.J., Cairns, V., Fox, G.A., Gilman, A.P., Peakall, D.B., Piekarz, D., Van Oostdam, J.C., Villeneuve, D.C. and D.C. Williams. 1991b. Toxic Chemicals in the Great Lakes and Associated Effects. Volume II. Effects. Pub. Govt. of Canada, 210 pp.

Armstrong, R.W. and R.J. Sloan. 1980. Trends in levels of several known chemical contaminants in fish from New York State waters. Bur. Environ. Protection, New York Dept. Environ. Conservation Report.

Borgmann, U. and D.M. Whittle. 1983. Particle-size conversion efficiency and contaminant concentrations in Lake Ontario biota. Can. J. Fish. Aquat. Sci. 40: 328-336.

Connor, D.J. and J.P. Connolly. 1980. The effect of concentration of absorbing solids on the partition coefficient. Water Res. 14: 1517- 1523.

Durham, R.W. and B.G. Oliver. 1983. History of Lake Ontario contamination from the Niagara River by radiodating and chlorinated hydrocarbon analysis. J. Great Lakes Res. 9(2): 160-168.

Frank, R. 1981. Pesticides and PCB in the Grand and Saugeen River basins. J. Great Lakes Res. 7: 440-454.

Frank, R., Sirons, G.J., Thomas, R.L. and K. McMillan. 1979. Triazine residues in suspended solids (1974-1976) and water (1977) from the mouth of Canadian streams flowing into the Great Lakes. J. Great Lakes Res. 7: 131-138.

Frank, R., Thomas, R.L., Holdrinet, H., McMillan, R.K., Braun, H.E. and R. Dawson. 1981a. Organochlorine residues in suspended solids collected from the mouth of Canadian streams flowing into the Great Lakes, 1974- 1977. J. Great Lakes Res. 7: 363-381.

Frank, R., Thomas, R.L., Braun, H.E. and T.T. Davies. 1981b. Organochlorine insecticides and PCB in surficial sediments of Lake Michigan (1975). J. Great Lakes Res. 7: 42-50.

Gummer, W.D. 1979. Pesticide monitoring in the Prairies of Western Canada. Water Quality Interpretive Report No. 4. IWD, Western and Northern Region, Regina, 14 pp.

ILEC. 1988 and 1989. Survey of the State of World Lakes. Parts I and II. Pub. ILEC/UNEP, Otsu, Japan.

Kaiser, K.L.E., Lum, K.R., Comba, M.E. and V.S. Palabrica. 1990. Organic trace contaminants in St. Lawrence River water and suspended sediments, 1985-1987. The Fate and Effects of Toxic Chemicals in Large Rivers and Their Estuaries. Science of the Total Environment, 97/98: 23-40.

Kaiser, K.L. 1974. Mirex: An unrecognized contaminant in fish from Ontario. Science 185: 523-525.

McCrea, Robert C., Fischer, John D and Kenneth W. Kuntz. 1985. Distribution of organochlorine pesticides and PCBs between aqueous and suspended sediment phases in the lower Great Lakes region. Water Poll. Res. J. Canada 20(1): 67-78.

McCrea, R.C. and J.D. Fischer. 1984. Design and testing of an aqueous phase liquid-liquid extractor (APLE). Inland Waters Directorate, Ontario Region, Water Quality Branch, Burlington, Ontario.

Pavlou, S.P. and R.N. Dexter. 1980. Thermodynamic aspects of equilibrium sorption of persistent organic molecules at the sediment-seawater interface: a framework for predicting and distribution in the aquatic environment. In: Contaminants and Sediments, R.A. Baker (*Ed.*), Ann Arbor Science Pub., Ann Arbor, Mich, pp. 323-329.

Pereira, W.E., Rostad, C.E. and T.J. Leiker. 1990. Distribution of agrochemicals in the lower Mississippi River and its tributaries. 1990. The Fate and Effects of Toxic Chemicals in Large Rivers and Their Estuaries. Science of the Total Environment, 97/98: 41-54.

Strachan, W.M.J. 1988. Atmospheric deposition of organic pollutants. Lakes Research Branch, Current Research, 1987-88, pp. 122-124.

Strachan, W.M.J. and S.F. Eisenreich. 1988. Mass balancing of toxic chemicals in the Great Lakes: The role of atmospheric deposition. IJC Report, Pub. IJC, Windsor, 113 pp.

Whittle, D.M. and J.D. Fitzsimmons. 1983. The influence of the Niagara River on contaminant burdens of Lake Ontario biota. J. Great Lakes Res. 9: 295-302.

World Resources 1990-91. A report by the World Resources Institute. 1990. Pub. WRI/UNEP/UNDP, Oxford University Press.

CHAPTER 7

OTHER ORGANIC TOXIC SUBSTANCES

José A. Catoggio

7.1 INTRODUCTION

Organic toxic substances (excluding pesticides or herbicides which were discussed in Chapter 6) found in lakes and reservoirs originate from a variety of sources. All of them are anthropogenic, thus differing from inorganic toxicants. Their effects vary according to their pollutant features(1) and environmental conditions(2). However, quite different residence times may correspond to the same input or inflow of each substance and, consequently, accumulation in water (where it implies greater immediate danger - be it because of direct consumption or because of bioaccumulation and bioconcentration along the trophic chain) or in sediments. Eventually, through these pathways they may pollute groundwater.

7.2 SOURCES

From a generic viewpoint, it is possible to distinguish between non-point, distant sources (whatever their original configuration -- single, line, area -- may be) and close, nearby, or even local sources. The input of toxic substances may be continuous (e.g. sewers) with discharges which may follow a given pattern or rhythm (hourly, daily or longer timespans), or it may be discontinuous (in this case, most often because of spillage or some other kind of accident) or periodical (as is the case with emissions from stacks, or liquid effluents from continuous or batchwise technological processes). Finally, it is necessary to distinguish the original sources from those within a given chain of activities liable to release toxic pollutants, such as transportation, storage, use, waste, disposal or recycling.

It is possible to tentatively classify toxicants according to the type of activity which generate them, as follows:

7.2.1 Urban sources

Domestic pollutants, released into lakes and rivers via wastewater drainage and sewers, may contain a series of organic substances of various toxicity levels. Among these it is possible to find solvents from paints, markers, cosmetics, adhesives, and the like; aerosol propellants

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(1) Namely vapor pressure, solubility, stability -- both physical and chemical -- activity coefficient, diffusion and adsorption behavior, toxicity level derived from its molecular structure, active functions and their spatial orientation, in the case of isomers.

(2) Namely the hydrogeological characteristics and hydrological regime of the system, plus the effect of meteorological agents such as rain and wind,and climatic agents such as temperature, luminosity, and relative humidity.

(nowadays mostly based on butane or other substitutes of the chlorofluorhydrocarbons, the use of which has been restricted under the Montreal Protocol); and even, in some cases, non-biodegradable surfactants.

Another source of urban contamination is rain drainage. Rain drainage carries pollutants -- gases, vapors, liquids or particulate matter -- taken by rainfall from contaminated air. These pollutants can include volatile solvents used in dry cleaning, products of domestic burning (heating or cooking), effluents from small workshops, effluents and emissions from gas stations, and so on.

Even in areas of very dry climate, where rain is scarce, aerosols and suspended particulate matter, especially that of large particle size and density, will deposit either directly on water bodies or on vegetation and soil. Through them they may pass to an aquatic environment.

An approximate idea of the amount of biodegradable organic substances in a water body can be found by the BOD/COD (biochemical oxygen demand/chemical oxygen demand) ratio.

7.2.2 Extractive and primary industrial sources

A number of activities and services directly related to urban areas produce large amounts of organic effluents. These include poultry raising, pig farming, dairies, slaughterhouses, packing houses and other intermediate industries processing natural raw material without too many modifications. In addition, cane or sugar beet processing, pulp and paper, fruit packing or canning, cotton or wool combing, distillation of essences and even tanneries all produce effluents which may include a large amount of organic matter in either dissolved or suspended form. Some organic substances thus discharged in the aquatic environment are biologically active (enzymes and, at times, hormones or alkaloids may be present as well as microorganisms and, eventually, larvae of parasites which are often pathogenic). These present dangers both to drinking water supplies and recreation activities (skin exposure).

Even though they are quite localized, extraction industries -- which are ordinarily located far from large population settlements -- also produce toxicants. Extraction activities include the exploitation of naturally active principles (e.g. alkaloids) and oil extraction from sites near lakes. In these instances additional precautions are required when dealing with the inherent problems of management, transportation, storage and use of the extracted substance.

7.2.3 Manufacturing and synthesizing industrial sources

Industries which process organic raw material or synthesize organic derivatives tend to be the most important sources of organic compounds. These compounds may themselves be toxic, or their intermediate products or byproducts, products of their degradation (physical, chemical, biological), or their final wastes may be. Industries using coal or petroleum, as well as petrochemical industries, deserve special mention here as major sources of toxic organic substances.

7.2.4 Other sources

Fermentation-based industries (including biotechnology) come under this category. The natural raw materials used generally include wastes from other industries or activities (most often agricultural) which range from alcohols and other rather simple and well-defined compounds, to antibiotics.

The wastes from agricultural activities can also be included here. In addition to agrochemicals (pesticides and fertilizers), large quantities of organic matter (dissolved or suspended), pathogens or products used to attack them, and, at times, toxicants produced by fungi (aflatoxins and micotoxins in general - aflatoxins are the most common micotoxins, mainly in food and feedstuffs) are all important organic toxic substances.

Finally, the sediments at the bottom of water bodies can be included because simple mechanical perturbation (dredging, waves) and/or biological activity (through the activity of benthic fauna and worms living in the sediment) can provoke their removal and recycling in a sort of feedback effect after the pollutants have been deposited and accumulated.

7.3 STORAGE

Negligence or excessive overconfidence of personnel in charge of toxic substances may result in accidents which can have very serious implications for ecosystems and human health. The same also holds true for the storage of toxic substances, through the various distributing agents along the production train from the factory to the consumer. The degree of danger naturally depends on the physical state and features of the hazardous product. Strict requirements are generally imposed for their localization, together with various security measures (similar to those for the prevention of fire and explosions), restrictions on reservoir or container dimensions and materials, and very strict control on their handling and operation.

Nevertheless, accidents may occur with the volatilization of substances which then enter into the environment through leakages directly to water bodies, to air or soil and, through them, indirectly to water.

7.4 TRANSPORTATION

Transportation is one of the most difficult steps to control, regardless of the mode of transport (by sea, river, land or air) or route adopted. Accidental toxic spillages during transportation are very well- known, and pose a danger to water bodies directly, and indirectly through rain wash-off and percolation through soil. Transportation procedures require the establishment of a risk "corridor" whereby the substance is subject to control from the point of loading to the place of unloading.

Leakage and contamination may also occur during routine maneuvers: loading or unloading, or the cleaning of tanks, bilges, containers, and fuel tanks in merchant vessels. Various international conventions prevent and control the spillage of oil or its derivatives, identify its origin, and impose penalties on those responsible for accidents. The transportation problem in lakes is ordinarily of lesser significance, primarily because of their size, with the exception of lakes of large dimensions and those in highly industrialized areas (e.g. the Great Lakes). The contamination caused by fuel and lubricants from motor-propelled leisure craft, which is of less importance in large lakes, may become a significant problem in smaller lakes.

7.5 USE

The variety of applications of potentially dangerous chemicals is much greater than the risk imposed by their generation. This is exacerbated in underdeveloped and developing countries where there are often neither suitable security regulations nor concrete possibilities of enforcing them. This applies to industries which use those substances as raw matter, intermediaries and final consumers of finished products.

This results in the entry of quite diverse toxic substances into the environment through air, water or soil. Lakes are one of the major sinks for these substances and the situation worsens when such lakes are located in plains where the water removal capacity is reduced. The same applies to reservoirs where water-depth favors some sort of stratification and the accumulation of persistent pollutants.

7.6 WASTES

The final wastes from toxic substances are unfortunately quite diverse and often pose a significant threat to the environment, human health and even life. The wastes from oil refineries and petrochemical plants are perhaps the most dangerous as some of the more toxic components are frequently very refractory. They are able to resist disposal techniques such as burning, unless combustion is conducted under very special conditions which can be satisfied in only a few facilities in the world.

7.7 PERSISTENCE, DISTRIBUTION AND FATE OF POLLUTANTS

The persistence in the environment of a given organic substance, be it toxic or not, fundamentally depends on three factors:

1. The properties of the substance, mainly its water solubility, vapor pressure and (physical, chemical and biological) stability.
2. Characteristics of the environment. In the particular case of lakes, surface area, depth, inflow and outflow rates, turbidity and the nature of the suspended particulate matter, dissolved oxygen (and oxidation potential), total concentration of salts (ionic strength) and biota (both amount and quality) are important.
3. Climatic characteristics such as temperature, luminosity, rainfall regime, and winds.

7.7.1 Properties of the substance

Under normal circumstances, substances will remain dissolved and diffuse within the water body until they reach equilibrium or steady-state conditions. There are, however, two processes which can cause the substances to exit from the system:

Volatilization or evaporation into the atmosphere. This is enhanced by high vapor pressure. The higher the ambient temperature, the greater the load of pollutant entering into the environment, and the smaller its concentration in air.

Precipitation or sedimentation. The sedimentation rate depends on the flow-rate, particle size and density, and depth of the water column. Sediments are sinks within which pollutants are buried, at least temporarily. When the pollutants are persistent, stable and being fed continuously into the system these sediments can reach worrying levels of toxicity.

The ease with which a pollutant is adsorbed on particulate matter gives a measure of the compound's hydrofobicity. A representative parameter of this characteristic is the partition ratio of the substance between n-octanol and water, Kow, which varies between 10^7 (for strong liophilic substances) and 10^{-3} (for those hydrophilic in nature), thus covering a range of 10^{10}. It is therefore more convenient both for calculus and graphing to use their respective logarithms, between 1 and 10.

Volatilization has been correlated with vapor pressure and adsorption and sedimentation, with interactions between the dissolved compound and the material constituting the suspended particulate matter. In both cases the distribution is within a heterogeneous system (air-water and water-solid respectively) which is separated by an interface through which the substance must forcefully find its way.

The criterium for assessing the magnitude of antagonistic processes involved in each case (evaporation-condensation and sorption-desorption respectively) has been unified in the concept of "fugacity capacity". Fugacity gives a measure of the tendency of the molecules of a given substance to "escape" from each of the phases or compartments where it is, thus ultimately being related to the vapor pressure of the pure substance.

Dissociation is a process which cannot be discarded. On the contrary, it may be more significant with increasing solubility of the toxicant in water. This would mean that the compound is polar, be it acidic or basic in nature. As such, the dissociation or ionization constant will be relatively high. It will increase with temperature and the salinity of the system (because of the decrease in the activity coefficients of the ions generated as a consequence of the dissociation) and it will certainly be affected by the pH of the aquatic environment.

Whatever enters into the system, if it does not leave it again (to air by evaporation or to the bottom as a sediment) must remain in the water column, be it as a molecular species or dissociated. This is of course only possible if there are no other simultaneous processes or reactions with equal or higher rates than simple (random) diffusion of the substance or advection.

On the other side, the ability of the dissolved substance to change or enter into reactions will largely depend on its stability in relation to different agents and conditions. This is determined by the molecular structure, the functional groups or substituents, and their position and spatial distribution.

7.7.2 Characteristics of the Environment

The greater the total amount of water in the system, the slower the substance will diffuse. In the same way, the slower the water flowrate, the longer it will take for the solution to become homogeneous and the greater will be the possibility and probability of competitive phenomena and processes leading to the decomposition or transformation of the substance. It is clear that these hydrodynamic characteristics of the environment do not affect the pollutant concentration, beyond the modification of its temporal-spatial distribution.

One of the principal transformation processes is decomposition through sunlight (photolysis). This is generally induced by metallic ion traces, though in some cases it may be a direct process. The greater the amount of available energy, the greater will be the probability of the photolytic decomposition for the same kind of molecules. The efficiency varies for different substances according to their ability to profit from the available energy. This is the reason why this type of processes are only possible in the upper layers of the water column and decline rapidly with depth and turbidity.

Besides these strictly physical actions, others of a different nature -- physico-chemical, chemical and biological -- can take place in an aquatic environment.

It has already been said that the trend of a molecule to be adsorbed on particulate matter is proportional to its hydrofobicity: it also depends on the organic carbon content of the particles. The more turbid the system is, the greater the fraction of dissolved substance which will pass to the sediment. The sorption process can be physical or chemical in nature.

Even in neutral lakes, dissociation of polar compounds, especially those with alcoholic, acidic or phenolic functions with a common -OH with water molecules (R_1CH_2OH, R_1COOH, R_2COOH or R_2OH, where R_1 is an alkyl radical and R_2 is an aryl group) is favored through the formation of hydrogen bonds between water molecules and homologue organic functions. The pH of the system, naturally, will play a decisive role in the dissociation of acids and bases.

Besides these dissociation or ionization processes, accompanied by solvation or hydration, the water molecule or its ions may intervene as a reagent in hydrolysis reactions, as is the case with esters or epoxides, thus generating new species whose characteristics and behavior (including their ecotoxicity) may substantially differ from those of the "mother" molecule. These hydrolytic reactions may also be catalyzed.

The total salt concentration, on the basis of which the ionic strength of the system can be calculated, will affect every equilibrium, primarily when it increases beyond 10^{-1} M (molar). This occurs, for instance, in salty lakes, because of its effect on the activity coefficient.

According to the level of dissolved oxygen and the oxidation potential of the system, the processes leading to the oxidation of organic pollutants -- usually in the presence of trace elements and sunlight -- are favored. This way, the formation of epoxy-rings or even the division of the molecules is possible. This results in the formation of derivatives or fractions with different characteristics (including ecotoxicity) from those of the original molecule. On occasions, when the substances deposit in deep sediments under anaerobic conditions, reduction reactions may be favored.

Finally, biota (especially microbiota) may be considered as a kind of suspended particulate matter. Separated by an interface from the water body, they are amenable to sorption phenomena. However, taking into account the fact that the substances prone to deposit at interfaces are those which are less polar, it is possible that one of the following may occur:

1. The toxic substances may affect the microorganism. It can inhibit vital processes, development or reproduction, finally leading to death and extinction in the system. In this case, the disappearance of a link in the trophic chain can interrupt the cycle of predators dependent on the extinct species and cause some selective migrations; or
2. The substance may be metabolized, and the metabolites (many of which can still be toxic) may then be excreted again into the water body or accumulated in organisms on which species of increasing complexity feed; this is called bioconcentration. The substance may reach levels which, while not toxic for individual links along the chain, may definitely be toxic for terminal consumers, including humans. In the case where hydrophobic toxic substances are not destroyed by heat when cooked, they are ingested by humans and deposit selectively in fatty tissues and organs.

A bioaccumulation factor (BAF) has been established which gives a good idea of the fate of stable toxic substances in a water body. It allows the risk to which a population is exposed when consuming fishes or mollusks which have concentrated these toxicants from polluted aquatic environments to be calculated. In fact, as will be seen in the case of polychlorinated biphenyls (PCBs), this enrichment may even be selective among members of a given family of compounds.

7.7.3 Climatic characteristics and meteorological agents

Climatic characteristics undoubtedly affect the environment and define the scenario in which the described processes occur. They favor some processes, inhibit the progress of others, and modify the distribution of contaminants in the various compartments which integrate the system.

Temperature is the determining factor on which every equilibrium depends. Luminosity is decisive in photolytic processes. Rainfall can provoke the seasonal accumulation of airborne toxic substances in very contaminated atmospheric air and, at the same time, bring about the dilution of those already in the water body. Finally, winds can produce waves in large shallow lakes capable of disturbing sediments and causing the recycling of contaminants.

7.8 PROPERTIES, PREDICTION, MODELLING (TOXIC SUBSTANCES' DISTRIBUTION, RISK ASSESSMENT)

The most important parameters, phenomena and processes which affect the distribution of toxic substances -- their (physical, chemical and biological) stability and, consequently, their persistence in the environment -- have been mentioned and their effects briefly described. These parameters enable us to predict the behavior of different kinds of molecules and their resistance to destruction.

The most significant processes and reactions which distribute a toxic substance within the water environment have already been discussed. Others include:

1. solubility in solvents other than water or n-octanol
2. diffusion coefficients and time of residence in air
3. volatilization from soil
4. vaporization heat
5. heat capacity
6. inflammation point
7. vapors, liquids and solids vapor density
8. liquid (and, at times, air) viscosity
9. interfacial tension with water
10. thermal conductivity
11. refraction index and
12. dipolar moment of substances.

These are discussed more fully in the references.

On the basis of such parameters it is possible to predict the physico-chemical properties of a substance and, in some way, even their distribution among the abiotic and biotic compartments of a given system. The functional groups and substituents, their position and spatial orientation, and the ecotoxicological characteristics of different substances can all be predicted.

Finally the input, distribution and fate of toxic substances within the different environmental compartments, as well as the assessment of the risk which is implied by exposure to them, have been the subject of modelling (see references). Among the models, those using fugacities for the prediction of the distribution and persistence of a compound in the environment are particularly interesting.

7.9 PREVENTION POLICIES (CLEAN TECHNOLOGIES, PROPER EMISSION CONDITIONS, TREATMENT OF EFFLUENTS AND WASTE DISPOSAL)

Undoubtedly the safest and most economical means for avoiding the release of toxic organic substances into the environment is through the use of technologies which do not generate them or through the minimization of their generation. This notion is however somewhat idealistic as the elimination or reduction of most toxic substances can be quite expensive. There are also cases where such substances (i.e. chlorinated dioxins) are produced during domestic and industrial waste incineration at 750°C or lower. Dioxins are extraordinarily persistent and refractory (primarily the tetrachloroderivative in positions 2, 3, 7 and 8), so that once they are introduced into the environment they remain there, immune to biodegradation, and appear accumulated in bottom-feeding fishes.

There are already too many operating industries involved, either directly or indirectly, in producing toxic substances. It is impossible to think of replacing them, particularly in underdeveloped or developing countries which have low per capita incomes and overwhelming foreign debts, the payment of which does not allow for sustainable development. In those cases, the only reasonable compromise is to try to alleviate the effects of available technologies with the application of techniques for minimizing the release of toxic pollutants.

There are three ways in which contaminants from factories are ordinarily introduced into the environment:

1. emissions of gas and particulate matter (fly ash, soot, etc.) produced in ovens or heating boilers and released from stacks;
2. liquid effluents discharged into surface water; and
3. solid or semi-solid wastes.

7.9.1 Emissions

One of the most serious problems is that of chlorinated dioxins. They apparently form whenever materials containing carbon, hydrogen, oxygen, nitrogen and chlorine are burnt at temperatures lower than 750°C. This being the case, instead of incinerating large volumes of wastes with very low dioxin content, it might be advisable to extract them, so as to reduce the amount of wastes to be burnt at very high temperatures. In such a case, it may be possible to extract the pollutants before their emission, by bubbling the cold gases through an extractant.

Ordinarily, contaminant gases are retained in bubblers or packed columns charged with antagonistic reagents: bases (e.g. lime) for acids, reducing agents for oxidants and vice-versa (e.g. H_2S oxidation with sulfur recovery). In other cases, the situation becomes much more cumbersome: for instance, when there are hydrocarbons in combustion gases, it is necessary to increase the proportion of air (or oxygen) in the burning mixture.

Methods for restricting the emission of particulate matter include filter bags, sinuous paths, electrostatic precipitators, and coalescence by ultrasonics.

The location and dimensions (mainly the height) of stacks is a decisive factor. Correct siting and height (taking into account the prevailing winds, distance from urban zones, and the nature and characteristics of the suspended particles) can limit the exposure for populated areas and water sources.

7.9.2 Liquid effluents

Effluents from oil refineries and petrochemical industries are among the most difficult to handle. A number of treatments are applied to them which include:

1. physical treatment (filtration, phases separation, eventual extraction, sedimentation, aeration, clarification by passing them through filter presses, etc.);
2. chemical treatment (basically neutralization, most often with the addition of salts of hydrolizable polyvalent cations such as aluminum (3+) to favor the formation of flocs on which contaminants adsorb and finally sediment); and
3. biological treatment (percolation through beds or towers with activated sludge, optional lagoons, stabilization ponds, etc.).

These treatments can recover significant amounts of hydrocarbons and the effluent quality can be improved until it matches the standards not only for total hydrocarbons but also for dissolved oxygen and chemical oxygen demand (COD).

In some cases, especially where effluents with a high organic content are involved, it may be advisable to use alternative depuration techniques, solvent extraction, adsorption on active carbon and oxidation with chlorine or ozone. Using ozone, the formation of persistent chlorinated compounds can be avoided, even with substances of low molecular weight which might have withstood other previous treatments.

7.9.3 Solid wastes

When treating effluents it is clear that, as a consequence of separation processes, solid or semi-solid wastes remain. These have to be disposed of, almost always as hazardous wastes, because of their high polycyclic aromatic hydrocarbons (PAH) content. Cementation techniques apparently have proven unsuccessful, and incineration is difficult since PAHs require temperatures of 1200-1400°C to be destroyed. The wastes cannot, however, be stored indefinitely. Therefore, some viable and efficient procedure needs to be investigated.

A possible, though controversial, alternative is aerobic biodegradation by land-farming. The reasons against it are related to land availability, the risk of leaks during transportation and, sooner or later, the accumulation of heavy metals in lixiviates. It has also been suggested that high frequency radiation or electric discharges can thermally destroy PAHs in situ in contaminated soils or dump sites.

It may be concluded that whatever the physical state, origin and eventual storage mode, transportation and use of any toxic substance, every release through leakage, spills or dumping should be carefully avoided. This should cover the whole process from formation to destruction or final disposal, taking into account the persistence and biodegradability of that substance. This highlights the need for adequate materials for containers and vehicles, and special precautions during storage and transportation in relation to the substance's characteristics such as volatility, fluidity, flammability, risk of explosion, etc.

7.10 REPRESENTATIVE EXAMPLES OF FAMILIES OF TOXIC ORGANIC SUBSTANCES

It is estimated that more than 4,000,000 organic compounds are known. A very high percentage of these are synthetic, and even though their formulae are established, very little is known about their ecotoxic behavior and metabolism. Less than 60,000 are used frequently.

Three important families of toxic substances are discussed below: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated dioxins (tetrachloro-derivatives, TCDD, being the most important among them). They are included here because of their relative ecotoxic and mutagenic (carcinogenic and teratogenic) effects, and because of their widespread distribution.

7.10.1 PAHs

PAHs are the most toxic among the hydrocarbon families. They may be considered as constituents of a typically anthropogenic family, and are formed during the distillation of coal. They appear in both coal and oil coke, being concentrated in tar and pitch and at the "bottom" of quenching operations in petrochemical industries. PAHs are also found as minor components of exhaust gases from diesel motors and cigarette smoke.

Several PAHs are proven agents of human cancer. Cancer of the scrotum has long been known as a professional disease of chimney-sweeps. Benzo(a)pyrene is used as a reference or standard. Their mutagenic activity is attributed to a given spatial configuration, so that stereoisomers may behave quite differently. Carcinogenicity of active species is linked with spatial structures capable of forming cycles with protein functions in the bodies of people who inhale or ingest them.

All PAHs are solid (the first term being naphthalene) and scarcely soluble in water. Almost immediately after being formed and released into the air they adsorb onto airborne particulate matter, especially on the carbonaceous fraction (soot) of very small size (aerodynamic diameter between 0.3 and 2-3 microns). Once adsorbed they are much more stable than pure compounds, and are resistant to oxidation and nitration reactions to which they would otherwise be quite sensitive due to photochemical processes in the atmosphere.

7.10.2 PCBs

PCBs are also anthropogenic. Until recently in developed countries they have been used as isolating fluids in condensers for electric power transmission lines - unfortunately they remain in use in underdeveloped and developing countries - while present regulations levels for permissible applications have been lowered to the order of parts per million.

Unavoidably, in spite of their unfavorable heat capacity and vapor pressure, they slowly volatilize, sorbing on airborne particulate matter. This is deposited by rainfall, and the PCBs enter into water courses and bodies where, because of their hydrophobicity, they finally sediment and consequently may be ingested. They are selectively accumulated and bioconcentrated, especially by benthic fauna (using PCB concentration in phytoplankton as a reference, concentrations increase by 500-2500 times in fish, depending on the species, and by 50,000 times in gull eggs) thus entering the food chain until being consumed by humans. They are deposited in fatty tissues in the same way as organochlorinated pesticides.

The brominated homologues, and their polybrominated derivates, PBBs, are used as flame retardants.

7.10.3 Chlorinated dioxins

There are 75 dibenzo-p-dioxins whose chlorinated derivatives (PCDDs) are known. They are generated when materials containing C, H, O, N and Cl are burnt at temperatures not higher than 750°C, while they are only thermally destroyed above 1000°C. They can also be formed as intermediate compounds in organic synthesis.

Highly toxic, as are their homologues, chlorinated benzofurans (PCDFs), they are responsible for some of the most sensational accidents of modern times (e.g. Seveso, Italy in 1976). They are also responsible for the toxic impurity of the 2,4,5-T herbicide, which was a component of the famous Agent Orange used as a defoliant in Vietnam, and whose use was denounced during the occupation of Afghanistan and the Kurd genocide in Iraq.

This list could be lengthened to include a wide range of organic compounds. UNEP permanently updates a very important data bank on toxic substances, the International Register of Potentially Toxic Chemicals, in Geneva (see Appendix). The data bank contains information on different tests run mostly in aquatic environments, making use of various species and the ecotoxicity of registered compounds under diverse conditions.

REFERENCES

United Nations Organization, "Engineering Equipment and Automation Means for Waste-water Management in ECE countries" (Part II), ECE/ENG. AUT./18, Vol. II, UN Publication no. E.84. II.E.23.008508 (Part II), New York (1984).

United Nations Environmental Programme:

(a) "Residue Utilization Management of Agricultural and Agro-industrial Residues (An Overview)", UNEP/Industry Program (1977).
(b) "Guidelines for Post-Harvest Food Loss Reduction activities", UNEP/Ind.& Environ. Guidelines Series, Paris (1983) - ISBN 92-807-1066-4.
(c) "Regional Workshop on Agricultural and Agro-industrial Residue Utilization in Latin America and the Caribbean. (Workshop Report), UNEP/IEO, Santiago, Chile, 16-19 July 1984 (1984).
(d) "Environmental Aspects of the Pulp and Paper Industry. (An 0verview)", UNEP/Ind. Program, Paris (1977).
(e) "Environmental aspects of the Pulp and Paper Industry (A Technical Review) UNEP/Ind. Program, Paris (1977).
(f) "Environmental aspects of the Sugar Industry" (An Overview)", UNEP/IE0, Paris (1982) - ISBN 92-807-1046-X
(g) "Environmental Aspects of the Petroleum Industry (An 0verview)", UNEP/IEO 40-40 Series I-I, Paris (1978).
(h) "Environmental Aspects of Iron and Steel Production (An 0verview)", UENP/IE0 (1984) - ISBN 92-807-1087-8.

International Maritime Organization, Regulations for the Prevention of Pollution by Oil." (Articles of the International Convention for the Prevention of Pollution from Ships, 1973 and of the Protocol of 1978 relating thereto). Annex I of MARPOL 73/78 including proposed amendments and Unified Interpretation of the Provisions of Annex I), London (1982), reprinted 1985.

Ibid., "Guidelines IMO/UNEP on the Application of Dispersants for hydrocarbons spillage and Environmental Conditions", London (1983) - ISBN 92-801-3078-I.

United States of America Environmental Protection Agency.- "Chemical Emergency Preparedness Program (Interim Guidance). Rev. 1, USA/EPA 9223-0-1A, Washington (Nov. 1985).

UNEP.- "APELL, Concientizaci6n y preparaci6n para emergencias a nivel local (Un proceso para responder a los accidentes tecnol6gicos)" UNEP Publ. no. E.88.III.D.3 (1989 - ISBN 92-807-1185-7 (00900 P).- English version *Ed.* 1988.

Lyman, W.J., Wm. F. Reehl & D.H. Rosenblatt, *Eds.*, "Handbook of Chemical Property Estimation Methods (Environmental Behavior of Organic Compounds)", McGraw-Hill Book Co., New York (1982) - ISBN 0-07-039175-0.

U.S.E.P.A.- "Rates, Constants and Kinetic Formulation in Surface Water Quality Modeling (2nd. *Ed.*) EPA/6O0/3-85/040, Athens, Ga., U.S.A. (1985).

Swann, R. L., & A. Eschenroeder, *Eds.*, "Fate of Chemicals in the Environment (Compartmental and Multimedia Models for Predictions)", ACS Symposium Series 225, Amer.Chem.Soc., Washington, D.C.(1983) - ISBN 0-8412-0792-5.

Liu, D., & B.J. Dutka, *Eds.*, "Toxicity screening procedures using bacterial systems", Marcel Dekker, Inc., New York (1984).

UNEP- International Register for Potentially Toxic Chemicals - 16, avenue Jean-Trembley, Petit-Saconnex, 1209 Geneve, Switzerland.

National Academy of Sciences "Particulate Polycyclic Organic Matter (Biological Effects of Atmospheric Pollutants)", Committee on Biological Effects of Atmospheric Pollutants, Division of Medical Sciences, National Research Council, National Academy of Sciences, Washington, D. C. (1972).

Gelboin, H.V., & P.O.P.Ts'O. *Eds.*, "Polycyclic Hydrocarbons and Cancer". Vol. 3. Academic Press Inc., New York (1983).

"Chemical Engineering News" - "Dioxins (Special issue), Vol. 61, no. 23, "Chem. & Eng. News", Amer. Chemical Society, Washington, D.C. (June 6, 1983).

CHAPTER 8

TOXIC SUBSTANCES MANAGEMENT PRINCIPLES DERIVED FROM EXPERIENCE WITH WATER QUALITY MANAGEMENT IN THE RUHR RIVER BASIN

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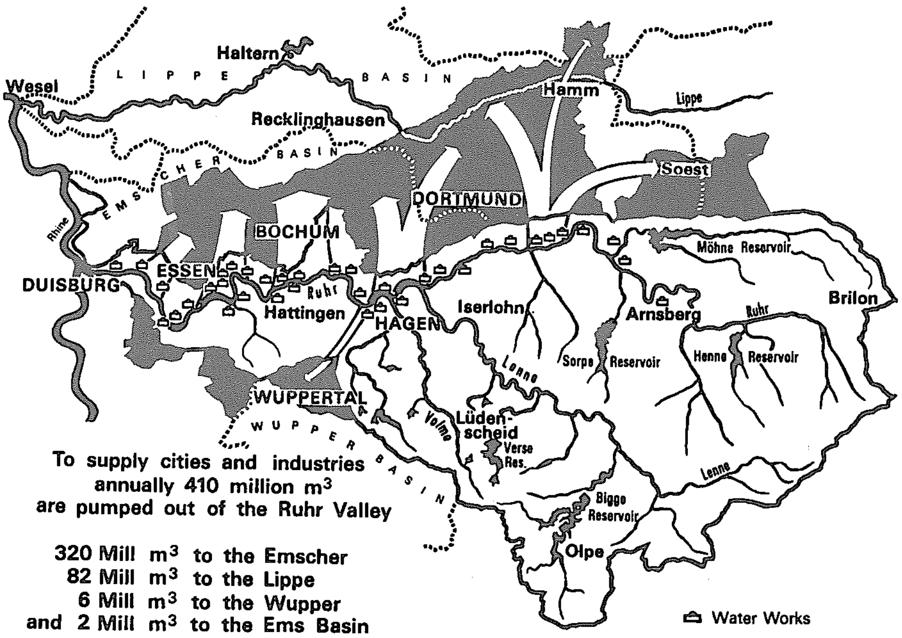
8.1 INTRODUCTION

The catchment area of the Ruhr River, a tributary to the Rhine River, covers about 4 500 km^2. The long-term average flow of the river (length 217 km) is 75 m^3/s. The Ruhr River is the main source of drinking and process water for the population and industries in this densely populated industrial area. About 6 million people live there and to supply the inhabitants of adjacent river basins (e.g. the Emscher basin) more than 300 million cubic meters of water are exported annually across the watershed border and are thereby lost from the Ruhr system (Fig. 8.1). Some 14 reservoirs with a total storage capacity of 471 million m^3 are operated to augment low flow.



To supply cities and industries annually 410 million m^3 are pumped out of the Ruhr Valley

320 Mill m^3 to the Emscher
82 Mill m^3 to the Lippe
6 Mill m^3 to the Wupper
and 2 Mill m^3 to the Ems Basin

Fig. 8.1 Ruhr River Drainage Basin and drinking water supply area

The Ruhr River and its tributaries receive treated wastewater from 2.12 million people and 1.7 million industrial population equivalents. The wastewater (337 million m^3/year) is treated in 116 plants (Fig. 8.2).

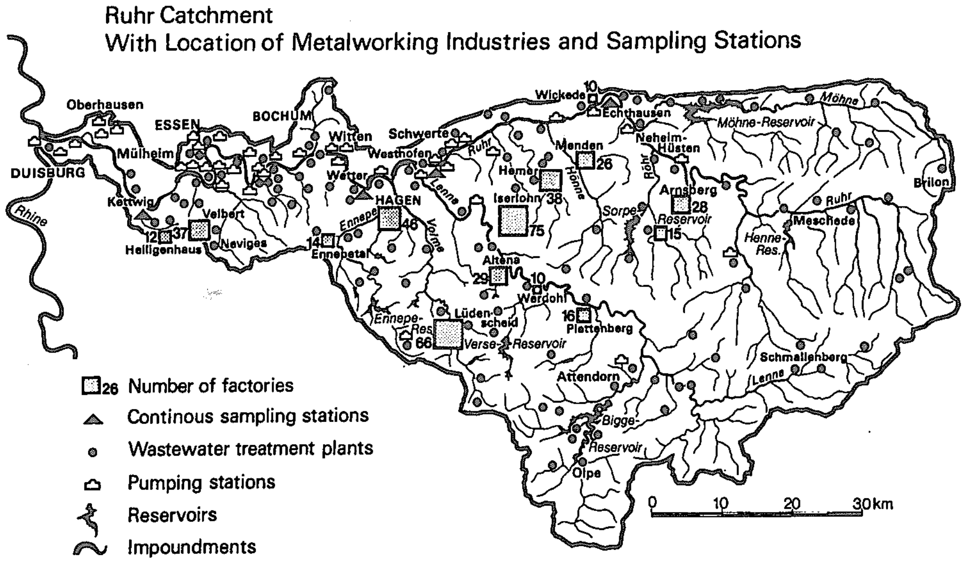


Fig. 8.2 Ruhr River drainage basin with wastewater treatment plants and industrial works

A total of 2 million m^3 of wastewater sludge has to be treated annually. Numerous iron and steel works, rolling mills, wire mills, pickling plants and about 250 electroplating plants are situated in the Ruhr River basin (Fig. 8.2). Moreover 11 textile-, 8 paper- and 6 leather industrial plants produce or handle more or less toxic substances. The industrial wastewater is - after detoxification - predominantly discharged to municipal sewerage systems and finally treated with domestic wastewater.

Since the wastewater pre-treatment of the mostly small or medium sized industrial plants is difficult to control and disturbances in the operation occasionally occur, thorough investigations into wastewater discharges, river water quality, control and avoidance measures are necessary as a prerequisite of toxic substance management in an industrialized river basin.

8.2 MONITORING AND SURVEILLANCE

The following results of short term monitoring, routine surveillance and long-term investigation programs shall exemplify the methodological approach, assets, limitations and success of control and abatement measures. From these experiences of the Ruhr River Association (RRA) principles for toxic substances management are derived.

Special toxicity problems may arise from emission of **heavy metals** (HM) (e.g. electroplating), cyanides (e.g. tempering), adsorbable organic halogens (AOX) (e.g. pulp and paper production), salt and **PCBs** (e.g. coal mining), **pesticides** (e.g. from agriculture) and **ammonia** (e.g. from wastewater treatment).

These substances and compounds are included in the quality surveillance of river water and waste water analyses of industrial producers of concern. Frequent sampling and concentration measurements are **basic requirements to detect and quantify pollution sources.** Periodicity and locality of concentration peaks can give valuable information in this respect. **Monitoring** of chemical and biological parameters is carried out at 25 selected sites along the river. At one reference point near Essen, daily sampling (Monday - Friday) and short term analysis has been carried out since the early twenties (Koppe 1975). The ample and copious data base is being used for statistic evaluations, e.g. trend analyses and models.

In addition to the RRA monitoring program several water works contribute analyses of Ruhr water quality at the raw water intake sites. Water temperature, electric conductivity, oxygen concentration, pH, algal fluorescence and other limnologically relevant parameters are continually recorded at several monitoring stations. Some of the monitoring stations are combined with continuous sampling and storage devices. Heavy metals are preserved with acid, halogenated hydrocarbons are collected on XAD ion-exchange resins.

The chemical analyses of spot samples are supplemented by biological investigations of benthic macroinvertebrates. The indicator species concept can give information on long-term sapro-biological conditions and, in cases of reduced abundance or total absence of sensitive species, on toxic pollution. Some water works used fish monitor devices in the raw water intake as early warning systems against occasional pollution.

A **monitoring and sampling station** is operated at Fröndenberg by the RRA in cooperation with a water company, and the state authorities (Fig. 8.3). Situated at the River Ruhr between a major industrial polluter and a waterwork, the station has an automated bioassay with Daphnia as test organism (Fig. 8.4). Swimming activity is recorded and in cases of toxic inhibition an alarm can be signalized (Fig. 8.5).

AOX (Adsorbable Organic Halogens) is a parameter used for control of organic halogen contamination in water. It covers the total amount of organically bound chlorine and bromine, and the partial amount of organically bound iodine which can be adsorbed on activated carbon. The principle of determination of AOX is as follows: Acidification of the water sample with nitric acid. Stripping of the water sample (if appropriate) and combustion of volatile organic halogens in a separate step. Adsorption on activated carbon of the organic substance in the water sample. Displacement of the inorganic halogen by rinsing with sodium nitrate solution. Combustion of the loaded carbon in an oxygen stream. Absorption of the hydrogen halides and determination of their mass concentration, for example microcoulometry.

Fig. 8.3 Monitoring and sampling station at Fröndenberg

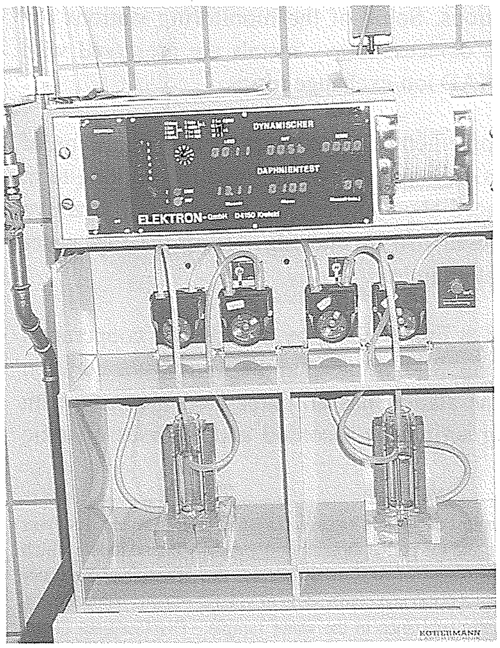


Fig. 8.4 Automated Daphnia toxicity test

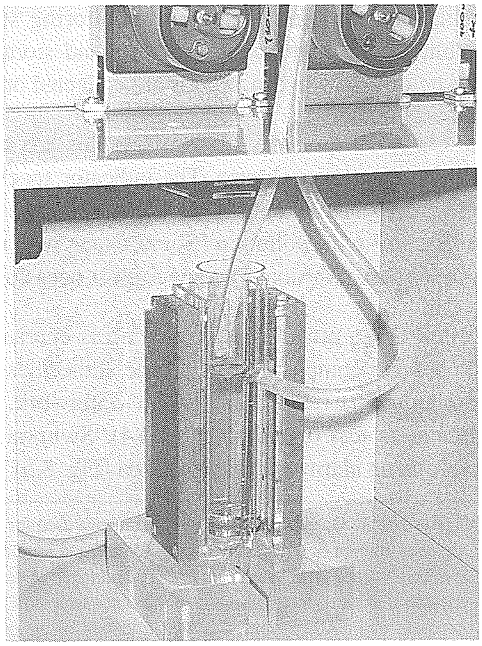


Fig. 8.5 Detail of Daphnia toxicity test

Long-term monitoring of heavy metals, PCB and pesticide **accumulation in biota** (water plants, fish, water fowl) is carried out at selected sites at irregular frequency.

The following diagrams and tables show exemplarily results of routine monitoring and special surveillance programs of heavy metal concentrations in Ruhr River water, wastewater, sediments, waste water sludges and biota.

Figure 8.6 shows a longitudinal profile of the sum of heavy metal (HM) concentrations in Ruhr River water. The first sampling point is near the source (above 200km), the last near the river mouth at Duisburg (5km). Peak concentrations were found below Oeventrop (160km) and below the inflow of the Lenne into the Lake Hengstey impoundment. This is the first indication of the pollution source, namely a pulp mill directly discharging into the river and various factories in the Lenne valley. The decrease in concentration is not only explained by dilution by unpolluted tributaries but (as shown later) by sedimentation of HM containing particulate matter. Comparing the long-term band (shaded area) of former measurements between 1965-1975 with the actual concentrations (1989) a reduction of HM concentration, especially in the Arnsberg area, becomes obvious.

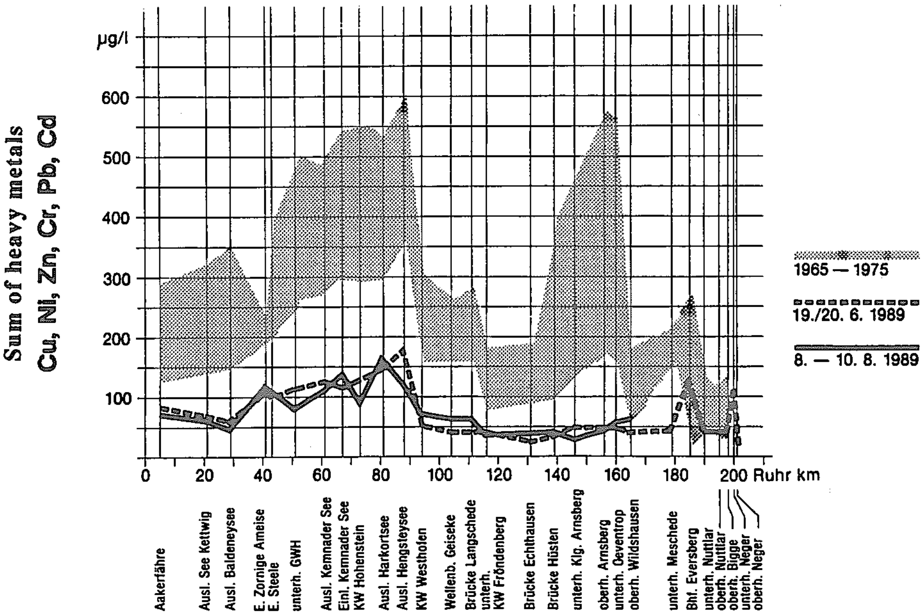


Fig. 8.6 Longitudinal profile of heavy metal concentrations (sum) in Ruhr River

Figure 8.7 shows the statistical distribution (as cumulative frequency) of selected HM in the Ruhr River near Essen. The deviation from log-normal distribution gives an indication of various non-natural pollution sources. The few extremely high concentrations, e.g. Cadmium >1 µg/l, probably result from accidental spills or illegal discharges.

As Figure 8.8 demonstrates, Cd-concentrations >1 µg/l have become extremely rare in recent years - not only in the lower (impounded) part of Ruhr River but also at Wetter (below the inflow of the Lenne tributary) where in the seventies 5% of all measurements exceeded 4 µg/l.

8.3 SYSTEM ANALYSES, TRENDS, BALANCES

8.3.1 HEAVY METALS (HM)

The correlation between water flow and HM concentration (Fig. 8.9) is a relevant part of the system analysis. It can serve as indication of the transport mode and of the introduction and mobilization mechanisms involved. The different behavior of the elements **zinc**, which shows increased concentrations with increasing water flow, and **nickel** showing a distinct decrease below 100 m^3/s means that **zinc is primarily particle bound** and remobilized by resuspension of sediments whereas **nickel is more easily leachable**, transported in solution and diluted by higher water discharge.

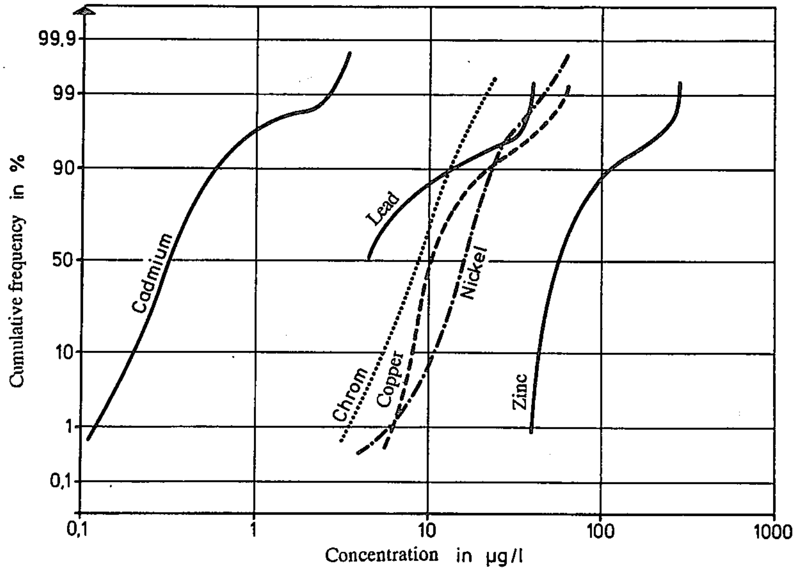


Fig. 8.7 Cumulative frequency of selected HM in the Ruhr near Essen 1986

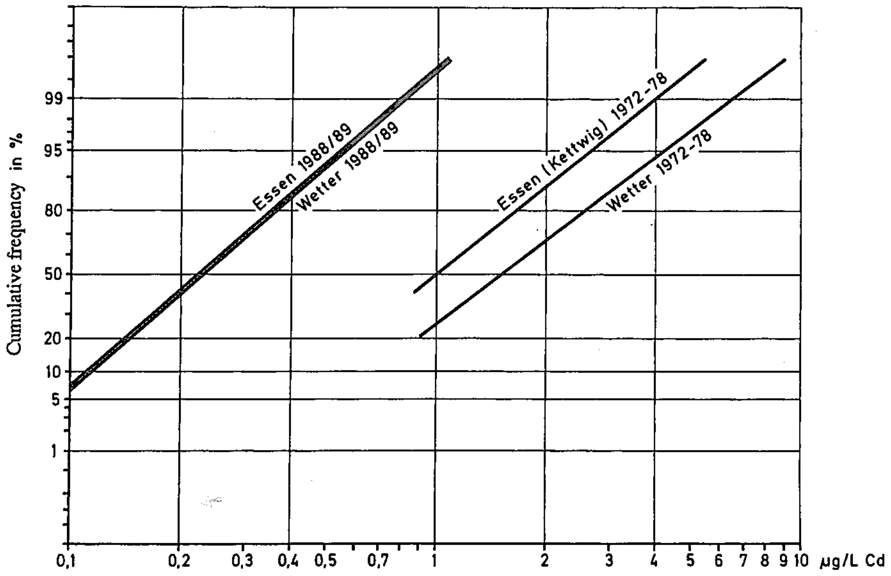


Fig. 8.8 Cumulative frequency of Cadmium concentrations in Ruhr River water at Essen and Wetter in the years 1972-78 and 1988/89

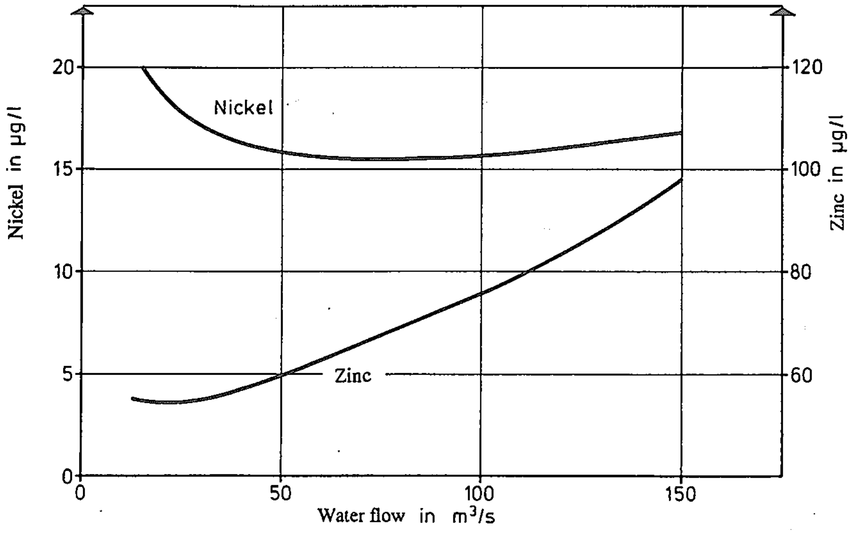


Fig. 8.9 Concentrations of nickel and zinc (µg/l) in relation to water flow (m^3/s) at Essen 1986

The success of **remedial and control measures** can best be demonstrated by a time series of nickel concentrations of Ruhr water at Essen (Fig. 8.10) from about 70 µg/l in 1973 to less than 15 µg/l in 1990.

Most important for the management of toxic substances in the Ruhr drainage basin is the **retention of HM in the waste water treatment process**, where HM are bound in or on the sludge. Figure 8.11 shows HM concentration in the influent of more than a hundred waste water treatment plants of the Ruhr River Association.

Table 8.1 indicates the mean HM concentrations in the effluent of RRA treatment plants.

Figure 8.12 (from KLOPP 1987) shows the dependence of HM retention from the influent concentrations. High retention rates can be achieved for lead, chromium and zinc. Nickel, however, can only be retained by less than 75% because of its high mobility in the liquid phase and relatively poor adsorption on solids.

Table 8.1 Mean HM concentrations in the effluent of the RRA treatment plants (KLOPP 1987)

lead	<10mg/1
nickel	12mg/1
copper	32mg/1
chromium	50mg/1
zinc	100mg/1

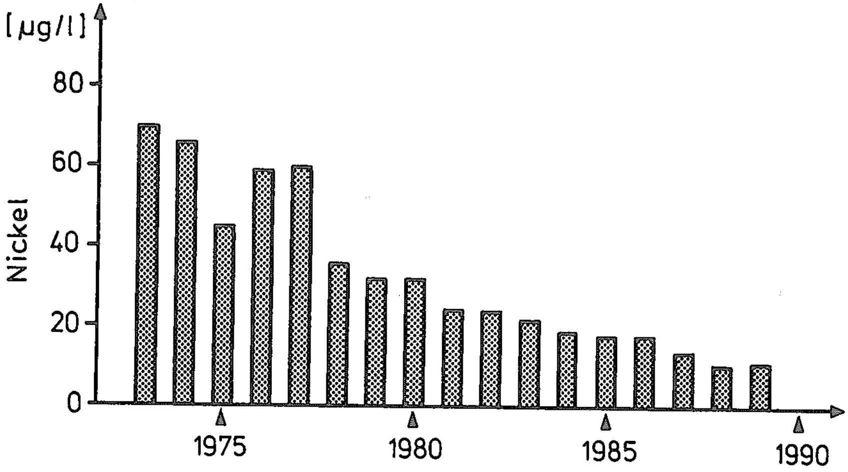


Fig. 8.10 Average nickel concentration of Ruhr River water measured at Essen 1973-1990

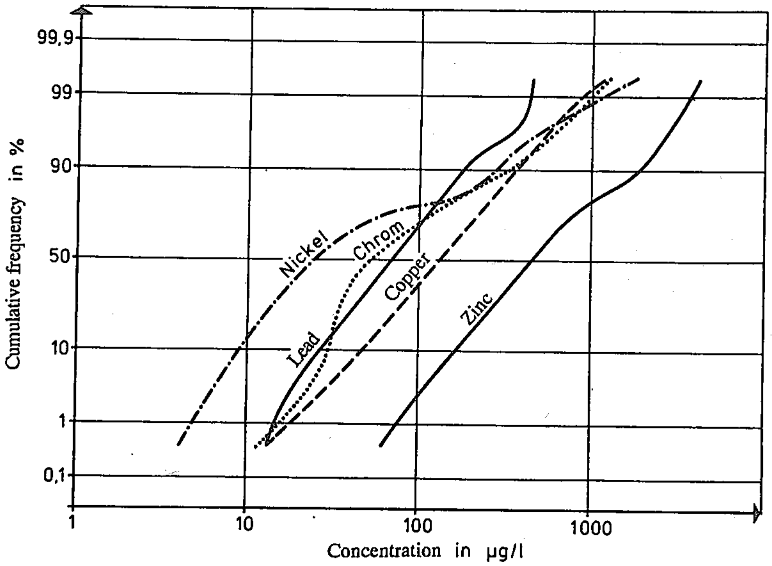


Fig. 8.11 Heavy metal concentrations (cumulative frequency) in the influent of RRA treatment plants in 1986

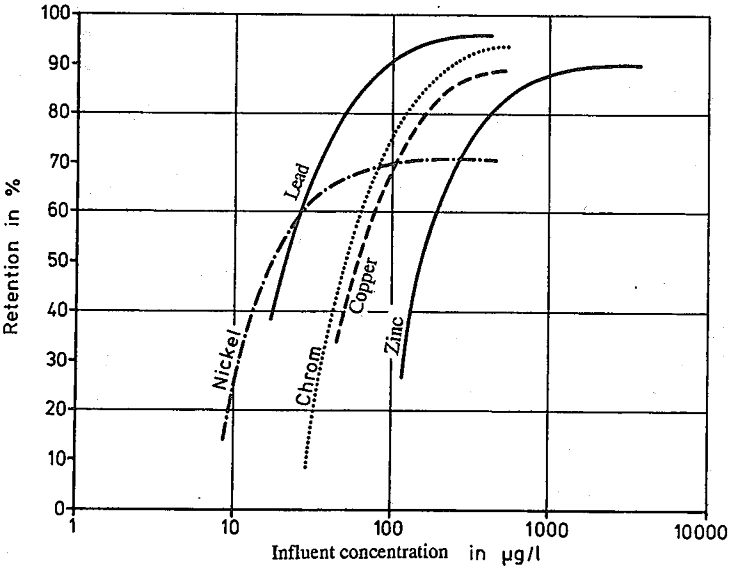


Fig. 8.12 Heavy metal retention in waste water treatment plants in relation to influent concentration

The elimination out of the liquid phase means accumulation in the solid phase. This may cause problems for the management of sewage sludges. In spite of the high nutrient values an **agricultural use of sewage sludge** is inhibited by HM exceeding the standards.

Table 8.2 shows the HM content (mg/kg dry weight) of sewage sludge of all RRA plants in comparison with German standards.

Table 8.2 Heavy metal concentrations in the sewage sludges of 116 municipal wastewater treatment plants in the Ruhr River basin and percentage of observance of the respectively valid standards for the treatment of plating waste water.

Heavy Metal	Standards for sewage sludges mg/kg d. s.	1975 – 1977			1986		
		50 Perc. mg/kg d. s.	90 Perc. mg/kg d. s.	frequency surpassed %	50 Perc. mg/kg d. s.	90 Perc. mg/kg d. s.	frequency surpassed %
Zinc	3 000	2 600	10 050	45	1 800	8 000	26
Chromium	1 200	254	4 000	17	99	1 600	12
Copper	1 200	680	3 100	18	500	1 800	16
Nickel	200	135	3 000	37	57	1 100	26

The **effluent standards for waste water** discharge into sewer systems have become more and more restrictive (Table 8.3).

Table 8.3 Development of German standards and guide values for wastewater discharge into sewer systems or surface waters respectively.

	normal values 1965	ATV-standard A 115 1970	ATV-standard A 115 1983	minimum requirements September 1984	minimum requirements September 1989
settleable solids ml/l	0.3	1.0	10	0.3	—
pH-value	6.5 — 9.0	6.5 — 9.5	6.5 — 10	—	—
chromium mg/l	2	4	3	2	0.5
copper mg/l	1	3	2	2	0.5
nickel mg/l	3	5	3	3	0.5
zinc mg/l	3	5	5	5	2
cadmium mg/l	3	—	0.5	0.5	0.2
silver mg/l	—	—	2	0.1	0.1
lead mg/l	—	—	2	1	0.5
cyanide mg/l	0.1	1	1	0.2	0.2
fish toxicity GF			—	dilution 8 times	dilution 6 times
COD mg/l			—	600	400
NH_4-N mg/l			200	100	100
fluoride mg/l			60	50	50
hydrocarbons mg/l			20	10	10
number of other parameters	—	6	13	4	10 among which AOX = 1 mg/l

The number of electroplating factories has decreased from 380 in 1966 to 250 in 1987. In 1966 only 20% of the works possessed detoxification devices or waste water pre-treatment. In 1989 when nearly all works were equipped, the requirements of effluent standards were met in more than 50% of cases. The non-observance quote has decreased considerably even if recent standards are more stringent, e.g. in the case of cadmium, where the standard was lowered from 3 mg/l to 0.2 mg/l. In spite of the improvements, until now only 30 - 40% of the sewage sludge can be used agriculturally (KLOPP 1987).

The HM-loading does not only result from industrial sources. Domestic sewage - primarily resulting from corrosion of household equipment and drinking water mains (zinced iron pipes) - already contains considerable heavy metal concentrations (Table 8.4).

Table 8.4 Heavy metal concentrations in domestic wastewater (from KOPPE & STOZEK 1990).

150 mg/l	copper
40 mg/l	nickel
100-1000 mg/l	zinc
30 mg/l	chromium
100 mg/l	lead.

Besides the HM retention in waste water treatment plants another important sink for HM, and thus a relevant mechanism in self purification processes, is the **sorption on particulate matter and the sedimentation of seston particles** in the impounded river stretches. Table 8.5 shows the HM content of Ruhr River seston indicating a considerable decrease in the years 1978 - 1989. The HM content, which according to the German Waste Disposal Ordinance should not be exceeded in soil, is added for comparison. The HM contents in Ruhr River sediments are tabulated for 3 locations measured in 1975 and 1989 (Table 8.6).

Table 8.5 Heavy metal content of suspended solids of the Ruhr River at Essen in 1978 and 1989 compared to soil standards of German Waste Disposal Ordinance 1982.

Year	1978	1989	Limit Concentration for agricultural soils
Heavy metal	mg/kg d. s.	mg/kg d. s.	mg/kg d. s.
Copper	1 200	560	100
Nickel	410	290	50
Zinc	5 200	2 660	300
Chromium	990	280	100
Lead	600	450	100
Cadmium	50	16	3

Table 8.6 Heavy metal content of Ruhr River sediments at 3 different locations in 1975 and 1989.

Location	Echthausen		Westhofen		Kettwig	
Year	1975	1989	1975	1989	1975	1989
Heavy Metal						
Iron	32 500	32 000	32 500	42 000	44 000	39 000
Zinc	2 180	1 280	1 970	1 670	3 880	1 580
Lead	680	260	450	370	680	280
Copper	233	100	565	730	1 090	270
Chromium	183	55	380	320	600	110
Nickel	128	71	219	140	440	120
Cadmium	15	5	17	5	37	7

The tolerated cadmium and zinc contents are near or even lower than the "natural" geogenic background. The HM content of waters and sediments of RRA reservoirs, which receive almost no industrial pollution and only few HM-loading from domestic or agricultural sources, is shown in Table 8.7.

Table 8.7 Mean values of heavy metal concentrations in waters and sediments of RRA-reservoirs.

	Zn	Cu	Ni	Co	Cr	Pb	Cd	Hg
water (µg/l)	9	2	4	3	—	2	0,4	0,004
sediment (mg/kg d.s.)	420	40	55	27	19	60	4,5	0,005

Standards, actual results and achievable concentrations of HM in the Ruhr River (Table 8.8) show the fact, that **in a densely populated country the natural conditions cannot be achieved even with extreme efforts in toxic substances management.** That means also that the dredged sediments in the lower part of the Ruhr River will not be adequate for agricultural use.

Table 8.8 Standards, actual results and achievable concentrations of heavy metals in the Ruhr at Essen.

	Imperative Values EC		Background-values (BLAK-QZ) 1989	Actual results Essen 1989	Achievable (no industrial wastewater)
	A 1 G	A 1 I			
Percentile	90	95	90	90	90
Heavy Metal	µg/l	µg/l	µg/l	µg/l	µg/l
Copper	20	50	2	25	23
Zinc	500	3 000	15	200	43
Nickel	30	50	3	30	7
Chromium	–	50	1	10	2,6
Lead	–	50	3	6	3,3
Cadmium	1	5	0,3	0,6	0,33

For the time being only 34% of waste water sludges do not exceed the HM-standards for agricultural use (KLOPP 1989).

One of the main objectives of toxic substances management in Ruhr River basin is the **reduction of the heavy metal loading at the source,** i.e. at the production site (electroplating workshops). It makes no sense to increase the retention efficiency of the RRA-treatment plants, because the **problem would only shift from the liquid to the solid phase** with the consequence of increasing disposal problems.

8.3.1.1 Balance account for HM in the Ruhr basin

Figures 8.13 and 8.14 from IMHOFF, KOPPE & DIETZ 1980 show the major sources for HM in the Ruhr basin: precipitation, ore deposits, runoff from fertilized land, wastewater from industries discharging (after treatment) either directly to the river or after pre-treatment to municipal treatment works.

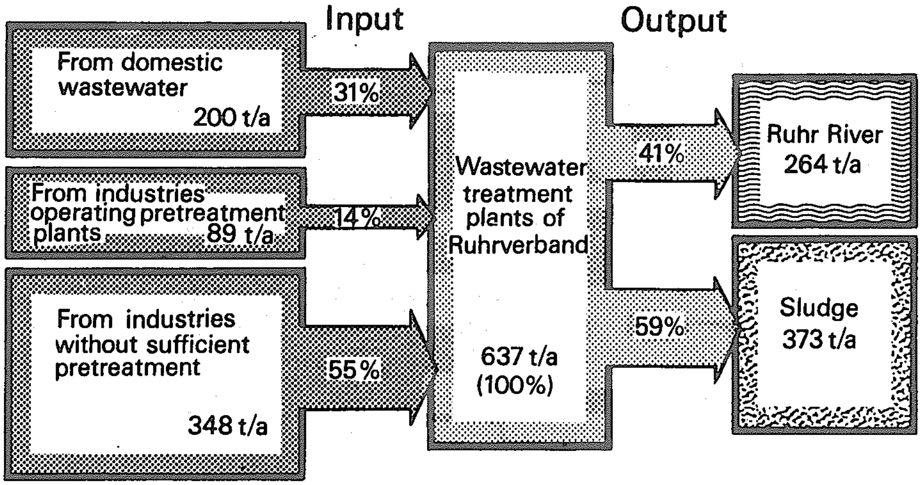


Fig. 8.13 Balance account of heavy metal loads run of Zn, Ni, Cu, Cr, Cd in the wastewater treatment plants of RRA (from IMHOFF, KOPPE, DIETZ 1980)

The contribution from agricultural areas and other non point sources was determined by the increase of HM concentrations in rivers without wastewater influence. The average soil erosion rate was 200 kg/(ha•a). This includes HM of about 0.05 kg/(ha•a). Analyses of the plant effluents revealed that 31% of the HM load in the plant inlets is supplied by domestic waste water, 14% by industries operating pre-treatment sufficiently and 55% by industries without sufficient pre-treatment.

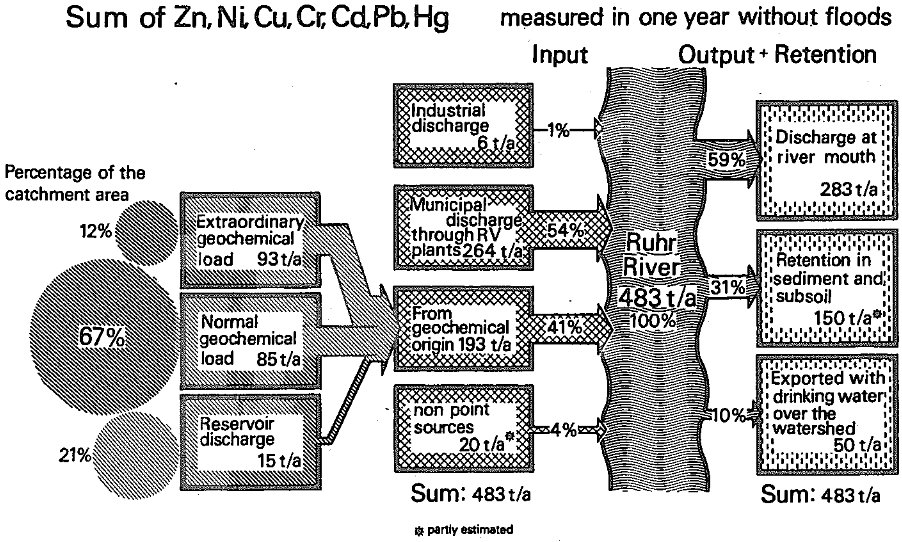


Fig. 8.14 Balance account of heavy metal loads in the Ruhr catchment (from IMHOFF, KOPPE, DIETZ 1980)

The balance for the entire river system (Fig. 8.14) indicates that 45% of the HM load is of geochemical origin and from non point sources, while 55% is discharged from municipal and industrial plants. Because of the HM reduction in the river impoundments and due to the considerable drinking water export to adjacent river basins, only 59% of the total HM load is measured at the river mouth. Sludge accumulation rates, determined by echo sounding and sediment analyses have shown that some 150 tons of HM are deposited annually.

The major portion of the HM load of the treatment plant inlets is discharged by industries without sufficient pre-treatment or illegal discharges of untreated concentrated wastes of industrial plants during night hours. These forbidden actions amounted to 30% of the total HM load of the river system.

Table 8.9 Relative HM contribution from industrial sources in municipal waste water (from KLOPP 1987).

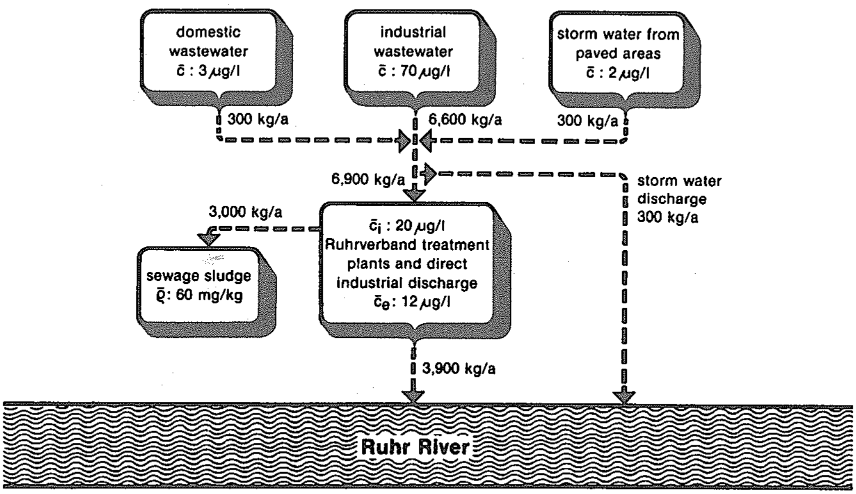
	Influent	Effluent
Copper	35%	34%
Nickel	80%	76%
Chromium	70%	37%
Lead	9%	9%

The origin of the elements and their relative fraction of the total load varies considerably. KLOPP (1987) computed the relative HM-contribution from industrial sources (Table 8.9).

Figure 8.15 shows the balance account of Cadmium loads in the Ruhr catchment.

Range of Cadmium Concentrations of Different Waters in the Ruhr Area

	concentration (µg/l)
groundwater	0.05 - 0.15
drinking water	0.05 - 0.2
falling rain at Essen	0.2 - 1.1
storm water flow from paved areas	1 - 10
seepage water from sewage sludge deposits	< 1
seepage water from industrial sludge deposits	5 - 50


Cadmium Emission from Ruhrverband Treatment Plants and Direct Industrial Discharge to the River

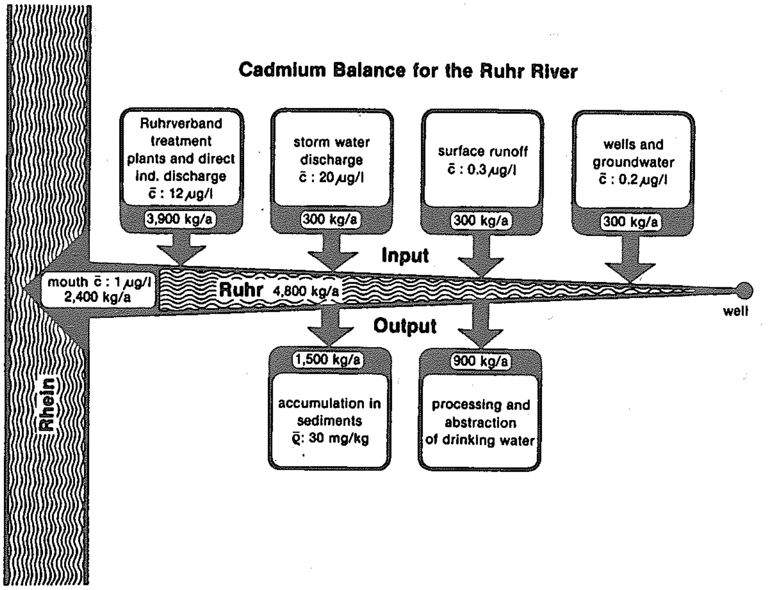

Cadmium Balance for the Ruhr River

Fig. 8.15 Balance account of Cadmium loads in the Ruhr catchment

8.3.2 CHLORINATED HYDROCARBONS (ADSORBABLE ORGANIC HALOGENS, AOX)

Another group of substances considered dangerous for human health and the aquatic biota, because of their poor biodegradability, their bioaccumulation potential and chronic toxicity, are **chlorinated hydrocarbons.** KLOPP and KORNATZKI published a **first balance of AOX in the Ruhr catchment area** in 1987 (Fig. 8.16).

About 20% of the annual AOX-emission into the receiving waters arose from municipal waste water plants, a third from a directly discharging pulp and paper work and nearly a half of the emission from diffuse sources caused by precipitation. The average AOX-concentration in falling rain is about 20 µg/l. The AOX load in run-off from paved areas is, astonishingly, nearly as high as' in municipal waste waters. A considerable part of the AOX-compounds in receiving waters may be of biogenic origin. Laboratory experiments showed the formation of halogenous organic substances when HCl gas reacts with unsaturated terpenes from natural spruce oil under exposure to sunlight (KLOPP & KORNATZKI 1987).

In 1986 a mean AOX-concentration in the Ruhr near Essen of 27 µg/l was measured. Some 5% of all measurements exceeded 45 µg/l. AOX is produced during the preparation of drinking water if the raw water is disinfected with chlorine or chlorine dioxide. The authors found an increase of AOX concentration in chlorinated drinking water of Essen by 15 µg/l.

A considerable portion of AOX results from the detoxification of cyanide from electroplating industries by oxidation with chlorine. Figure 8.17 shows a 5-fold increase of mean AOX concentration from 110 (50 percentile) to 550 µg/l if chlorine is used.

In 1990 the pulp and paper factory, previously (see Fig. 8.16) emitting 26t of AOX (chloroform) annually, closed down. A significant reduction in AOX concentration resulted as shown in Figure 8.18.

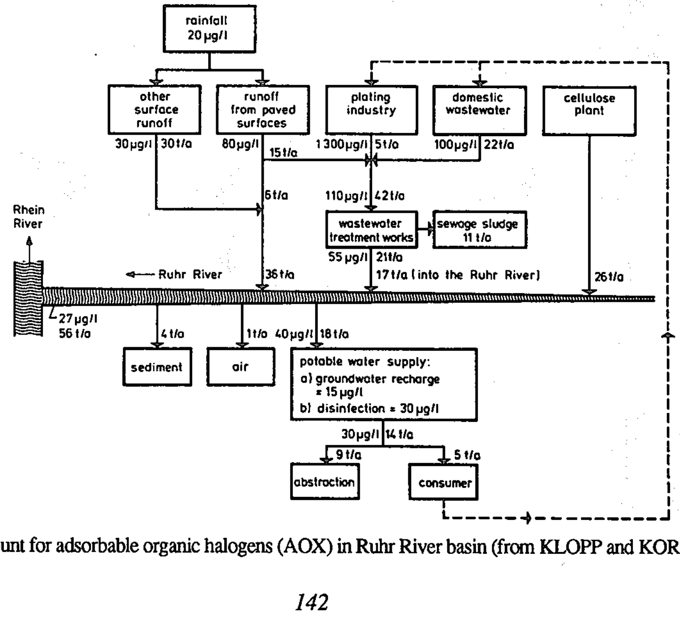


Fig. 8.16 Balance account for adsorbable organic halogens (AOX) in Ruhr River basin (from KLOPP and KORNATZKI 1987)

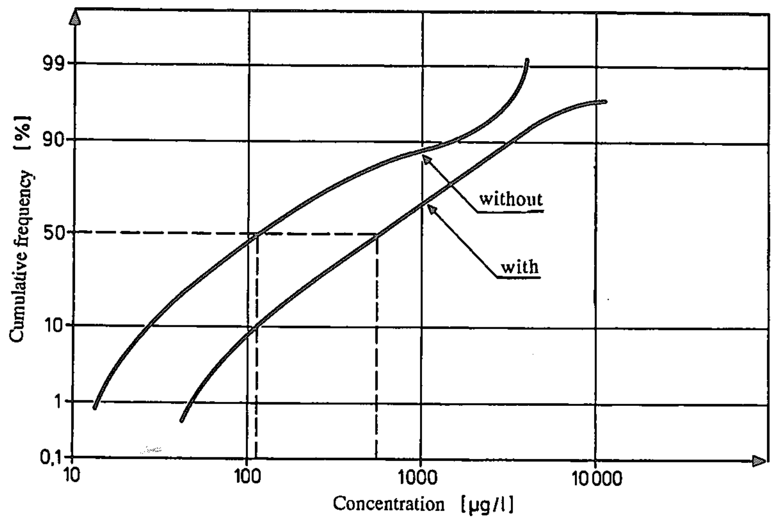


Fig. 8.17 Cumulative frequency of AOX-concentrations in the effluent of plating wastewater detoxification plants with or without cyanide oxidation by chlorine (from KLOPP & KORNATZKI 1987)

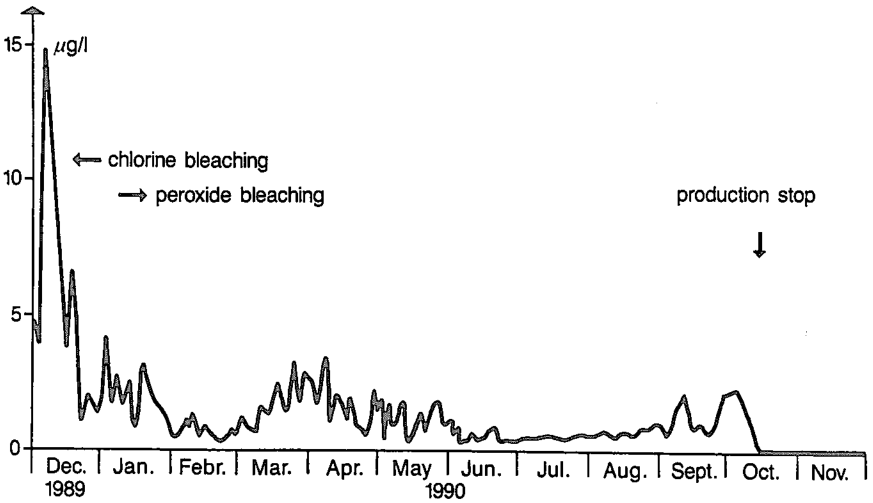


Fig. 8.18 Trichloromethane concentration in Ruhr River before and after closing of a pulp mill (Data provided by LWA Düsseldorf)

8.3.3 POLYCHLORINATED BIPHENYLS (PCB)

PCB-compounds, formerly used as nonflammable medium in electric transformers or hydraulic oils in coal mining, are extremely persistent. They accumulate in biota, especially in fatty tissues.

Because of its bioaccumulation potential and chronic effects they are considered to be hazardous to human health. As the Ruhr River is used intensively for hook and line fishing, PCBs are included in the RRA biomonitoring program. Figure 8.19 shows the PCB concentration in fish exemplarily as cumulative frequency of the most common product, Clophen A 60.

The PCB concentrations in edible parts of fish should not exceed 0.2 - 0.3 mg/kg fresh weight according to German food quality standards. All PCB (and HM) concentrations in edible parts of fish analyzed so far indicate that fish of the Ruhr River can be consumed without hazard to human health. Relatively high values, however, were found in past years for cadmium in fish liver and PCB compounds in fatty tissues of eels. Since PCBs had been substituted by related compounds (e.g. Tetrachlorinated Diphenylmethane, TCDM). PCB-concentrations have been decreasing considerably. TCDM concentrations in fish of the Ruhr River were below detectability.

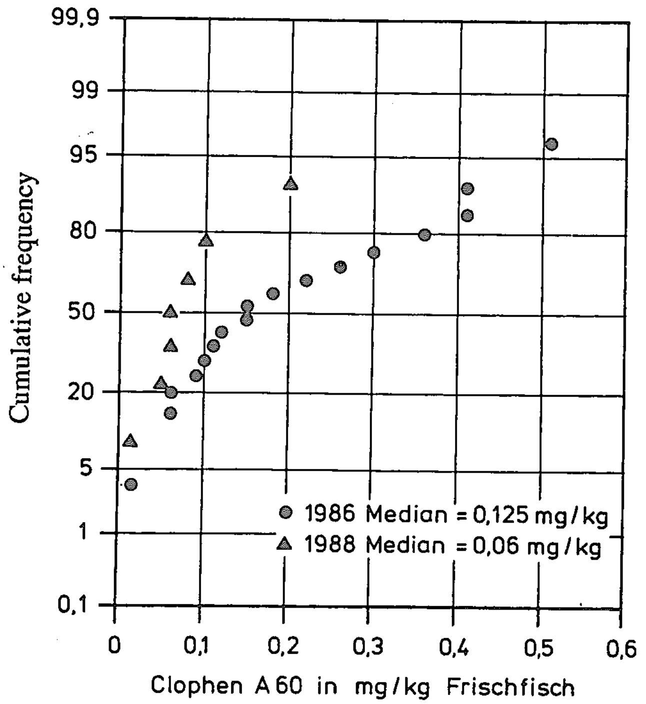


Fig. 8.19 PCB concentration (cumulative frequency of Clophen A60) in fish of Ruhr River (from Ruhr Quality Report 1988)

8.3.4 PESTICIDES

Pesticides are introduced into the Ruhr River mainly from diffuse sources. Some 35% of the drainage basin is used agriculturally. The herbicide **Atrazin** is applied especially on corn growing areas. **Simazin** is often used to prevent plant growth on railways, streets or paved areas. These herbicides are considered hazardous because of their persistence and their toxic potential. According to the German Drinking Water Quality Standard (1990) the concentration of single plant protecting agent is limited to 100 ng/l in drinking water. The sum of pesticides must not exceed 500 ng/l.

The analytics and control of these substances is especially important to safeguard adequate raw water quality. Figures 8.20a and 8.20b show space-time diagrams of Atrazin and Simazin concentrations in the Ruhr River. The distribution pattern of these two herbicides is obviously different. The major Atrazin peaks are observed in winter and late spring in the middle stretch of the Ruhr River, whereas Simazin is mainly found in summer with increasing concentrations towards the river mouth.

The distribution pattern may be indicative of the mode of application, mobilization and transportation of these substances. Atrazin, for instance, is used at the beginning of the vegetation period of corn. It is then partly volatilized and transported in the atmosphere and precipitated with the rain.

After the corn harvest the bare soil is extremely prone to leaching and erosion. This might be the reason for the winter peak in times of high water flow. It is precisely at this time that Simazin concentration is lowest due to dilution.

Additional steps in the drinking water preparation process, e.g. activated carbon filtration, are required to eliminate the pesticides and to meet the extremely low drinking water quality standard. **However it cannot be the duty of drinking water works to repair the consequences of agricultural production**. Since the pesticide loading originates from diffuse sources and cannot be controlled by water quality management of RRA, **legislative measures are necessary** if the farmers do not cooperate voluntarily. Since January 1991, the application of Atrazin is no longer allowed in the catchment area of a waterwork.

Sometimes less hazardous alternatives can be found through **cooperation between water quality management and agricultural consulting agencies.**

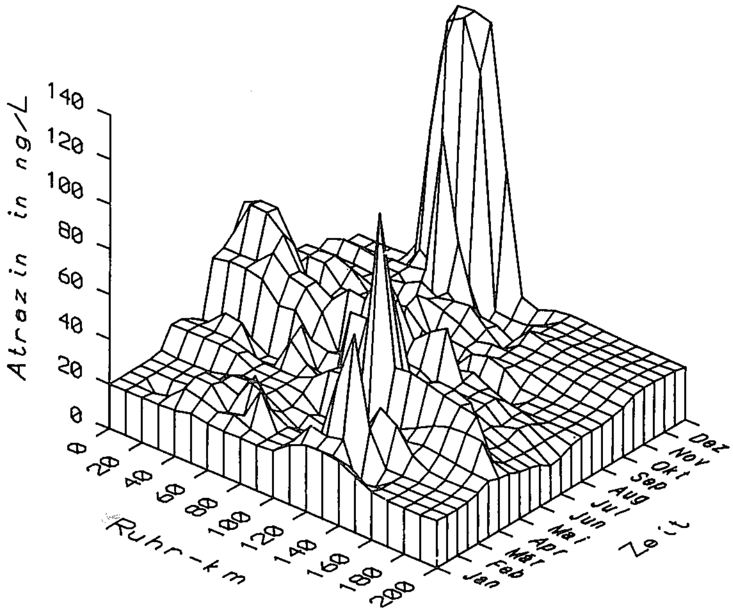


Fig. 8.20a Atrazin concentrations in Ruhr River at different locations during the year 1989

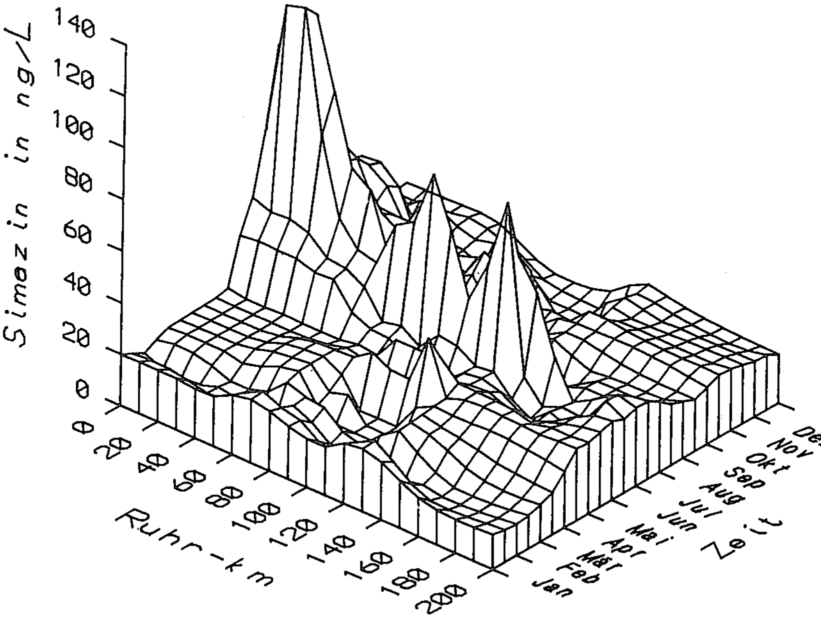


Fig. 8.20b Simazin concentrations in Ruhr River at different locations during the year 1989

8.3.5 AMMONIA

Ammonia is not only detrimental from the point of view of drinking water supply, but also toxic to fish if it is converted at high pH values to the unionized form NH_3. The European Community has issued fisheries imperative standards of 0.025 mg/l NH_3 or 1.0mg/l NH_4^+, respectively, for cyprinid waters.

Acute toxicity, that means fish kills, are to be observed at NH_3 concentrations exceeding 0.5 mg/l NH_3. The lethal concentrations with resulting fishkills have been observed in a few cases in an impoundment of Ruhr River (Lake Kemnade).

Increased mortality is also recorded fairly regularly in late springtime (May) at the weir of Lake Baldeney.

This "late spring fishkill" can be explained by the combined effect of spawning stress, extreme oxygen conditions (fluctuating from more than 20 to less than 5 mg/l), high ammonia concentrations (resulting from temperature inhibited nitrification of waste water) and high pH (resulting from photosynthetic carbon dioxide depletion). When these various biotic and abiotic influential factors coincide, fish life is endangered.

According to the revised First Sewage Administrative Ordinance, enacted in 1990, NH_4-concentrations in waste water effluents of plants > 5000 population equivalents should not exceed 10 mg/l. The RRA is going to operate its treatment plants with sludge loading of 5 0, 15 kg BOD/(kg DS•d) to enable nitrification and to meet the legal standards. The enlargement of treatment plants will require an additional investment of 750 million DM.

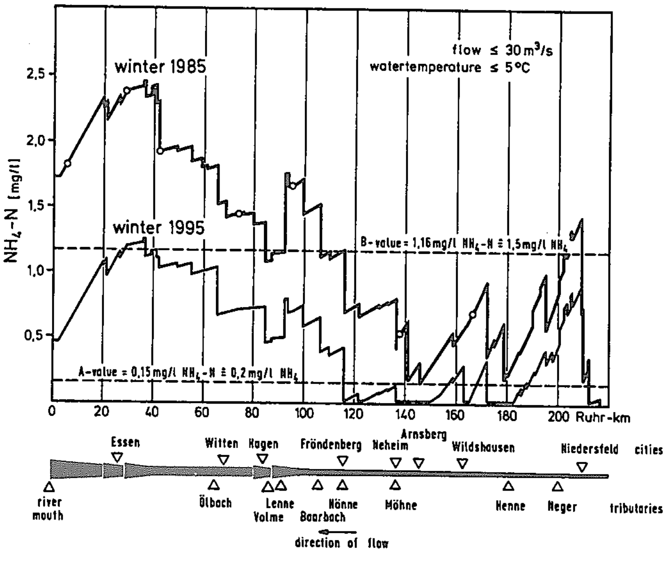


Fig. 8.21 Longitudinal profile of ammonia-nitrogen in Ruhr water

It is expected that the boundary value (B-value) of 1.5 mg/l NH_4, which is now often exceeded in the middle and lower reach of Ruhr in times of low flow conditions, will not be surpassed in the near future (Figure 8.21).

8.4 CONTROL AND ABATEMENT MEASURES

8.4.1 CONTROL OF COMPLIANCE WITH STANDARDS

The German Association of Waste Water Technology (ATV) has issued a Working Paper (ATV A 115) with guidelines for effluent concentrations. The number of workshops and factories exceeding the ATV-A 115 guide values by 3 times or more is shown in Table 8.10.

Table 8.10 Number of industrial plants exceeding the guide values of ATV A 115 (KLOPP 1989, supplemented).

year	number of works
1985	93
1986	88
1987	78
1988	64
1989	45

According to our experience the inadequate operation and maintenance of pre-treatment plants is the main cause for ineffective detoxification of industrial waste waters prior to discharge into the municipal sewerage. Improper operation and maintenance or illegal discharges, however, cannot be totally excluded. Therefore the **surveillance of industrial effluents is an important tool of toxic substances management.**

The analysis of deposits in the sewerage system and the application of so called "sewer detectors" - that are devices with ion exchange resins placed temporarily into the waste water mains below a suspected polluter - have been successful in detecting illegal discharges retrospectively and to track down and convict the emitter (KOPPE & JABS, 1987).

Intensified surveillance can influence effluent quality as shown in Figure 8.22 (from KLOPP 1989) for the development of nickel loading of sewage sludge during intensified surveillance and routine monitoring periods. During periods of intensified surveillance the volume of hydroxide sludges transported from an electroplating plant to the central detoxification and dewatering plant increased significantly (Fig. 8.23).

Flexible surveillance, i.e. intensified in cases of suspected or experienced problems and less frequent routine spot sampling 3 - 4 times a year, has proven to be **optimal with regard to expense in relation to yield.**

It is a great advantage that the majority of industries do not discharge directly into the river but indirectly via the municipal treatment plants. **The combination of pre-treatment at the production site and final treatment prior to discharge into the river ("double netting") increases the safety of the system considerably.**

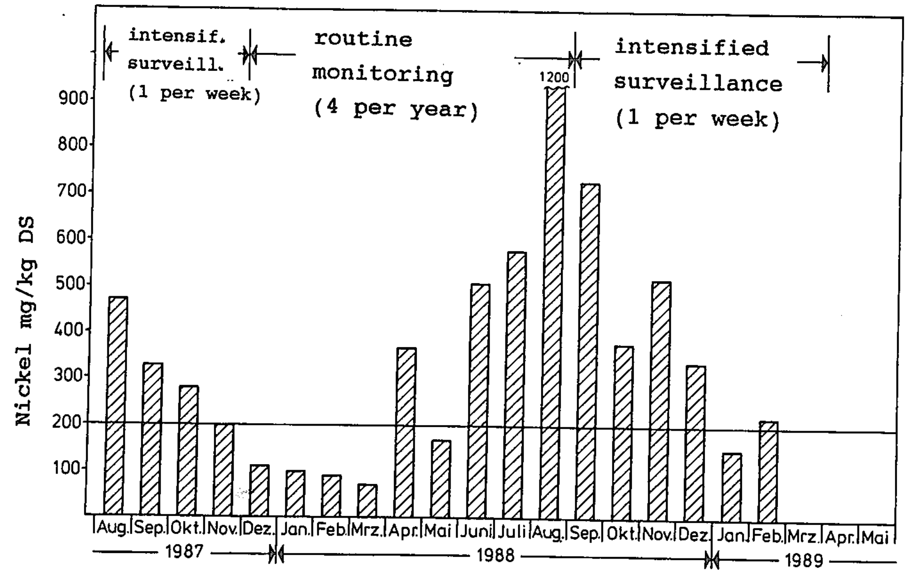


Fig. 8.22 Development of nickel loading of sewage sludge during intensified surveillance (1 per week) and routine monitoring (4 per year) (from KLOPP 1987)

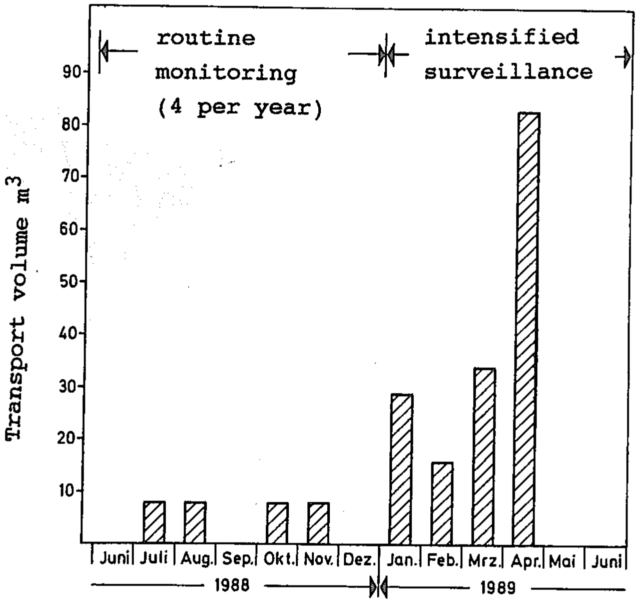


Fig. 8.23 Development of transport volume of HM-hydroxide sludges from a plating plant to the RRA detoxification and dewatering plant

8.4.2 CENTRAL DETOXIFICATION AND SLUDGE DEWATERING

In the Ruhr catchment there is a total number of 450 metal finishing establishments. Pickling and plating plants are obliged to pre-treat their wastes before discharge into the sewerage system (cf. Table 8.3). From the 237 pickling works some 9,000 tons of spent hydrochloric acid and some 7,000 tons of iron sulfate are collected annualy by the RRA and recycled to the chemical industry (IMHOFF 1989). The sale of the products covers only the transportation costs. But there is a considerable saving compared to chemical precipitation and disposal of resulting hydroxide sludge.

Adequate sludge treatment becomes a problem as in most facilities, especially in smaller workshops, the required space is not available. The Ruhr River Association (RRA) therefore constructed and operates two **central detoxifications and dewatering plants** for waste concentrates and sludges from pickling and plating shops (STÖLTING 1986; Fig. 8.24). Figure 8.25 shows the detoxification and removal scheme.

In the case of plating wastes it is most important to separate cyanide and chromium polluted wastewaters. The destruction of cyanides is effected mainly by oxidation with chlorine. Chromium is reduced with iron sulfate at a pH value of 2.5. After detoxification the different wastes are mixed and neutralized. Sludges are separated and thickened. For further concentration mostly filter presses are applied. Finally the sludge cakes are disposed of on controlled pits. Sludge deposits have a sealing to prevent seeping into the underground. As far as possible, surface waters are diverted. Drainage water is drawn off and treated in neighboring plants (IMHOFF 1989).

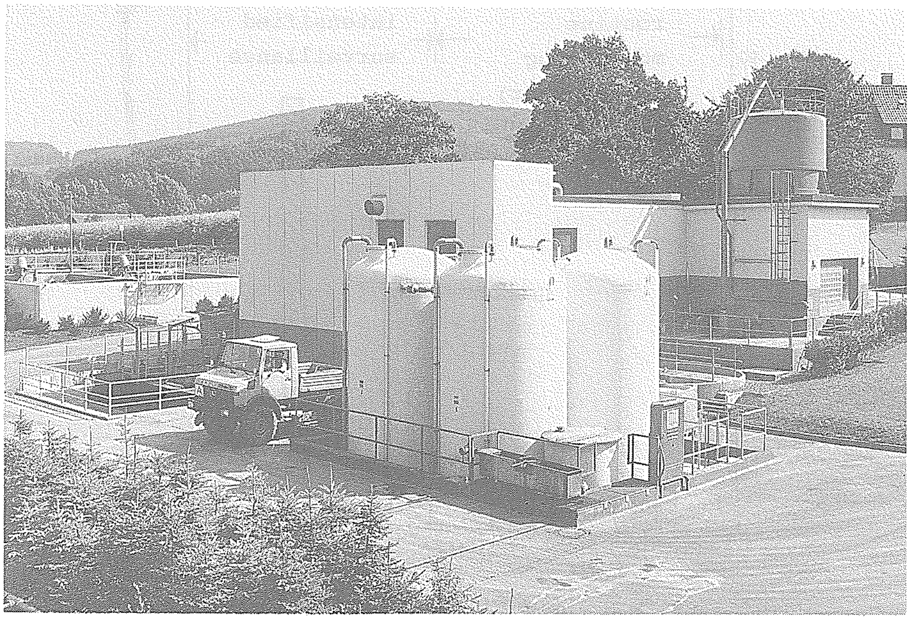
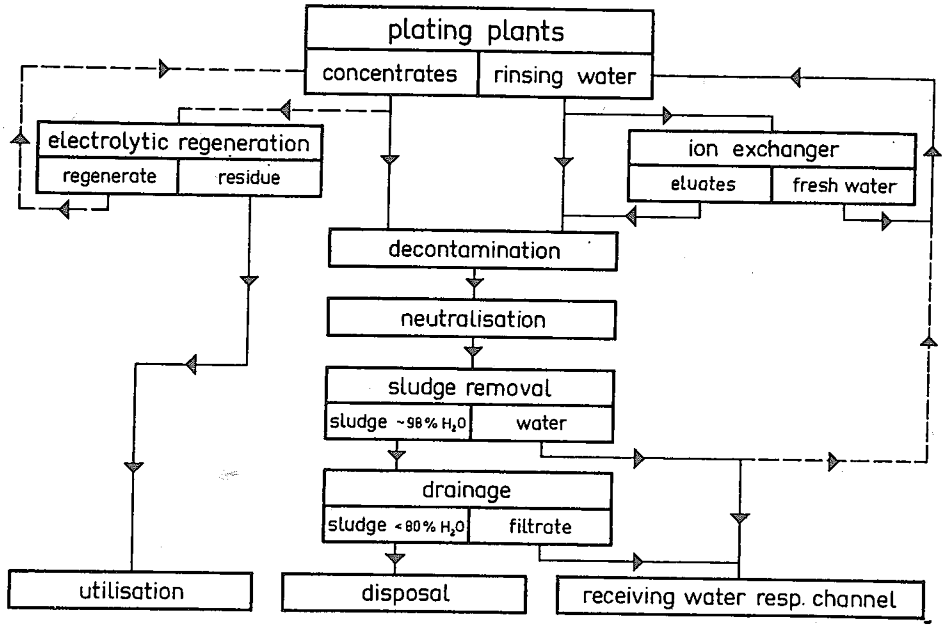


Fig. 8.24 Central detoxification- and dewatering plant of RRA at Iserlohn

Process Scheme for Treatment of Plating Wastes



Process Scheme for Treatment of Pickling Wastes

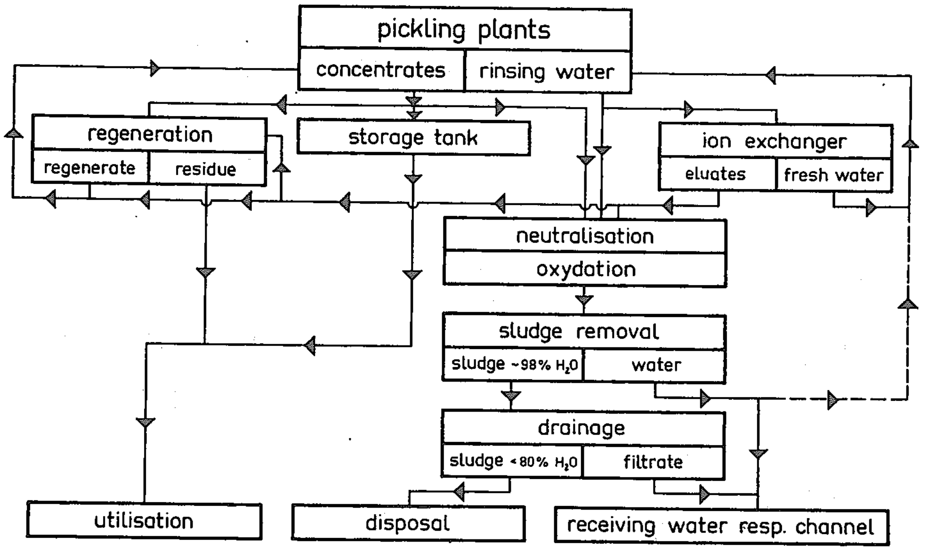
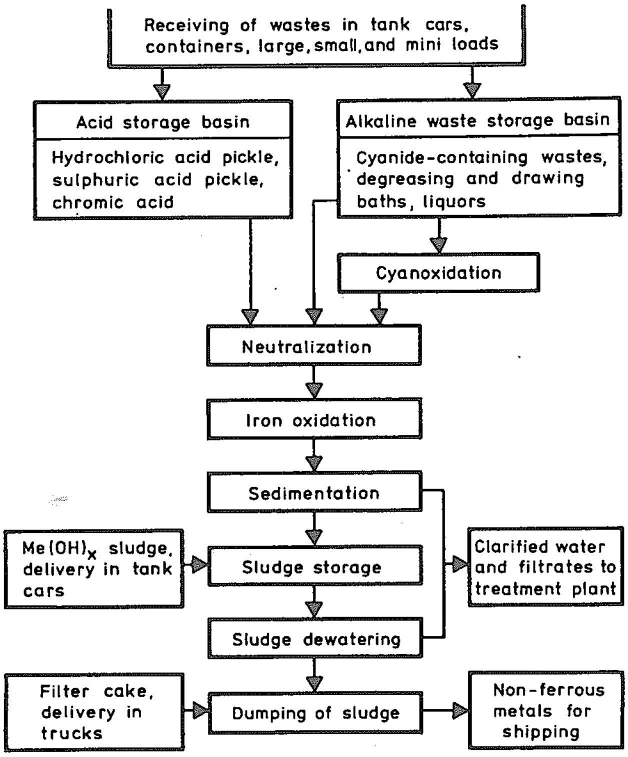


Fig. 8.25 Schematic diagram for the removal of toxic substances from electroplating and pickling plants

Fig. 8.25 continued



Schematic diagram of a central plant for the removal of toxic substances from electroplating plants and pickling plants

8.4.3 REMOVAL AND DISPOSAL OF CONTAMINATED SEDIMENTS

Sediments can be considered as the memory of a lake. Past pollution is accumulated and stored here (Table 8.11). The elimination from the water - functioning concomitantly with accumulation in the sediment - does not mean elimination out of the aquatic system. The final elimination is only achievable by removal of the sediment. This was done in 1983/84 when 750,000 m^3 sediment was removed out of Lake Baldeney by suction dredging. The sediment slurry, mixed with lake water, was transported through iron pipes to a deposit, situated 5 to 8 km upstream of Lake Baldeney. In order to save space, the deposition area was surrounded by dams. Soon after drying up of the soil surface, semi-aquatic and terrestrial pioneer plants, e.g. Phragmites, Bidens and Epilobium began to grow thus enhancing the drying process by evapotranspiration. In the meantime the deposit has overgrown densely with trees and shrubs, predominantly willow (Salix) species.

Table 8.11 Average HM content of Lake Baldeney sediment (KOPPE et al. 1983).

Iron	50080 mg/kg d.w.
Zinc	3540 mg/kg d.w.
Manganese	1299 mg/kg d.w.
Copper	727 mg/kg d.w.
Lead	525 mg/kg d.w.
Chromium	404 mg/kg d.w.
Nickel	312 mg/kg d.w.
Cadmium	36 mg/kg d.w.
Mercury	0.38 mg/kg d.w.

The experience of Lake Baldeney sediment dredging and disposal is now being advantageously applied to similar operations at other Ruhr River impoundments.

8.4.4 TOXICANT IDENTIFICATION AND WARNING SYSTEM

In a highly industrialized catchment area accidental or unlawful pollution cannot be totally excluded. Traffic accidents of tank lorries, leakage or spillover of tanks, illegal discharge of industrial or agricultural wastes occur from time to time. In 1989 the RRA was informed of about 50 cases (partly trifiling). About 50% were cases of oil spills, 30% were fish kills resulting from various reasons including "natural" causes, e.g. diseases, spawning difficulties, oxygen depletion. In most cases the causes of fish kills could be explained and the origin of pollution detected. Table 8.12 shows the major causes of fish kills and accidental water pollution recorded in the years 1980-1989:

Table 8.12 Causes of fish kills and accidental water pollution recorded from 1980 to 1989 (from the Ruhr Quality Report 1990, in preparation).

Oil	32%
Organic wastes	10%
Heavy metals	8%
Cyanides	4%
Acids/Bases	4%
Ammonia/pH + spawning stress	4%
Pulp and paper wastes	2%
Biogenic oxygen depletion	1%
Other	18%
Unidentified	16%

At total of 37% of the 182 reported cases effected fish kills.

When the RRA is informed, e.g. by police, fire brigade, local authorities or personnel of its own treatment plants - some co-workers serve as "river warden" for a certain reach of neighboring waters - an elaborated alarm plan is set into operation. Most important is the early warning and information of the drinking water works downstream. The alarm system is highly redundant. In addition to the police's, municipal authorities' or RRA alarm plans an information chain within the waterworks has been established.

The knowledge of flow velocity is necessary to indicate the expected arrival of a contaminated water body at the raw water intake. The RRA has conducted several **tracer experiments** with fluorescent dyes between selected points of the Ruhr River under various flow conditions in order to establish a hydraulic model (Fig. 8.26).

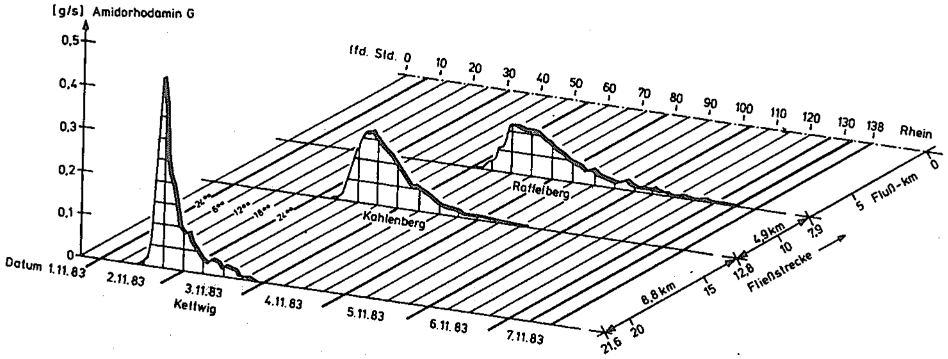


Fig. 8.26 Tracer experiment in Ruhr River between km 29.3 (Lake Baldeney weir) and 7.9 (Raffelberg weir) 10 kg Amidorhodamine G16 -

Sometimes, if the source of pollution and the cause of a fish kill is unknown, it is a challenge for the chemical analyst to identify the toxic substance(s) of concern. The RRA laboratory has developed an **identification strategy combining rapid bioassay procedures** (e.g. with daphnia, fish), **technical separation techniques** (e.g. adsorption, filtration, extraction), and **chemical analysis**. The identification scheme follows a "decision tree" procedure stepwise reducing the number of possible alternatives concerning the toxic agent.

8.5 LEGAL AND FINANCIAL ASPECTS

The Ruhr River Association is a self governing, state-controlled public body. Associates of the RRA are all communities and industrial companies contributing to the pollution of the Ruhr River and all water supply institutions benefitting from the water quantity and water quality management of the RRA. The cost for construction, maintenance and operation of waste water treatment plants and reservoirs are paid by the associates. The construction costs are partly covered by financial support of the state.

Since 1948 the RRA has invested approximately 1720 million DM. Currently 30% of the water pollution control expenses are paid by the waterworks. The remainder is collected from communities and industries according to volume and pollution load of discharged wastewater. The charges, which are computed by a sophisticated cost assessment rule including a BOD-inhibition bioassay for toxic substances can be enforced like a tax.

The RRA has to pay for the discharge of treated wastewater according to the German Law on Effluent Charges. Table 8.13 shows the equivalent pollution units for the parameters of concern. In 1986 nearly 19 million DM had to be spent for about 420,000 pollution units from 118 wastewater treatment plants of the RRA, 200 industrial plants directly discharging and 300 communities. Additionally 260,000 pollution units resulted from 1,300 stormwater discharges.

Table 8.13 Pollution units according to the German Waste Water Charges Act 1990.

No.	parameter	the following quantities are equivalent to each one pollution unit
1	COD	50 kg oxygen
2	phosphorus	3 kg
3	nitrogen	25 kg
4	AOX	2 kg halogen, calculated as organ. combined chlorine
5	metals and their compounds:	
5.1	mercury	20g metal
5.2	cadmium	100g metal
5.3	chromium	500g metal
5.4	nickel	500g metal
5.5	lead	500g metal
5.6	copper	1000g metal
6	fish toxicity	3000 m^3 of wastewater devided by the factor of fish toxicity "G_F"

8.6 PRINCIPLES DERIVED FROM THE RRA EXPERIENCE

In the preceding chapters the methodological approach of toxic substances management was described. Starting from

- **routine water quality surveillance,**
- **detection and quantification of pollution sources,**
- **long term monitoring of chemical and biological parameters,**
  advancing to
- **statistical analyses of trends,**
- **balance accounts** and
- **evaluation of control measures,** and finally
- **establishment and operation of detoxification plants**
  the feed back loop is closed with the
- **effect monitoring of the success of counter measures.**

As this concept has been developed, optimized and approved in long standing practice, some principles can be derived from this experience. These principles may be formulated by the following catchwords or captions.

8.6.1 "Avoidance comes before repair"

That means input control at the source of pollution instead of elimination later in the water cycle - for example detoxification of industrial wastes as much as possible at the production site, not in the municipal treatment plant or even in the water work.

8.6.2 "Kill the big pigs first"

This slogan is common and of long standing in water quality management. It means a reasonable balance between expense and yield of control and abatement measures. In other words: "balance account comes before rehabilitation".

A thorough system analysis has to evaluate the relative share, sources, sinks and effects of toxic pollution in order to integrate single solutions within the framework of an overall concept.

8.6.3 "Retention does not mean elimination"

This caption is exemplified by the necessity of removal of contaminated sediments in order to prevent the hazard resulting from remobilization of heavy metals accumulated and reversibly retained in sediments.

8.6.4 "Dilution is no solution for pollution"

This is true if the loading is considered, but toxic effects are primarily dependent on concentration. In some cases it might be advantageous to augment low flow by increased discharge from reservoirs, but this can only be done exceptionally, for instance in cases of accidental pollution. The interdependence of water quality with water quantity has to be regarded, planning the location of waste water treatment plants in order to protect small recipient waters to be charged with high concentrations.

8.6.5 "Compartment shifting is no final solution"

Since elimination of non degradable pollutants from liquids, e.g. water and wastewater, means accumulation in solids, e.g. sludge, sediments, problems might occur after sludge incineration or stripping of volatile pollutants during aeration.

8.6.6 "Redundancy increases safety"

This is a fundamental rule in toxic substances management. Discharge of industrial wastewater, even if detoxification devices are installed and operated, directly into the recipient waters is the exception in the Ruhr catchment. The RRA favours pre-treatment at the industrial production site and indirect discharge via the municipal sewerage and combined treatment with domestic sewage.

Facilities for intermediate storage and subsequent supplementary detoxification are kept in reserve in cases of occasional pollution of the influent to the RRA wastewater treatment plants. In addition to conventional mechanical and biological treatment, polishing lagoons are operated as a find treatment step and hydraulic buffer in cases of shock loadings.

8.6.7 "Supervision increases safety"

An obvious example for the increasing diligence coming into operation during and after intensified supervision of industrial detoxification plants was demonstrated (Figures 8.22 and 8.23) of proper maintenance and operation treatment plants and compliance with standards can be ascertained by a dual system of self surveillance combined with external supervision. Incidental means of voluntary self control and indicators for the performance of treatment plants are living fish in polishing lagoons.

8.6.8 "Polluter pays"

Pollution should be more expensive than purification. Levies are computed according to loading. Toxic substances, have to be included in the assessment by chemical analysis and/or biological assay. Example: German Waste Water Levy Act.

8.6.9 Quality objectives and legal standards are necessary as a challenge for water quality management

Unrealistic claims, however, overcharging the practical and financial means are counterproductive. Standards below background concentrations or below analytic detectability are not operable.

8.6.10 "Multiple use needs partnership"

The principle of cooperation is fundamental for the RRA's relation with its associates. Experienced members of the RRA staff offer advisory services to dischargers of hazardous wastes to cope with special problems concerning detoxification and disposal of wastes.

Waterworks, industrial producers and municipalities, that means receivers of and emitters into the Ruhr River water are associates. Their different interests have to be harmonized by the board of representatives and deputies. Mutual consulting and exchange of experience and information are required to cooperate and to find partnership with environmentalists, anglers, aquatic ecologists, recreational agencies, governmental authorities and other personalities and institutions interested in water quality.

This principle of cooperation has been successfully developed and applied since the Ruhr River - and Ruhr Reservoirs Association were founded in the first quarter of the century. It is a remarkable fact that these organizations, until now responsible for water quality management in the Ruhr District, were founded voluntarily and later established officially by a governmental act. The extremely difficult task of restoring and maintaining a good water quality in a small river draining a densely populated industrial area, and successfully coping with problems originating from the dual use of the Ruhr River for drinking water supply and waste water discharge has found more than regional recognition (BOWER *et al.* 1981; CLEARY 1983).

REFERENCES

Bower, B.T.; Barre, R.; Kühner, J.; Russel, C.S. & Price, A.J. (1981): Background of the Genossenschaften Ruhrverband and Ruhrtalsperrenverein in Incentives in Water Quality Management in France and the Ruhr Area Resources for the Future, Res. P.R. 24, ISBN 0-8018-2661-6

Cleary, E.J. (1983): Managing water resources: Lessons for the U.S., J. Water Poll. Contr. Fed. 55 (8), 1034 - 1041

Dietz, F. (1985): Gewässerbelastung durch EDTA - eine neue Herausforderung an den Gewässerschutz. Korrespondenz Abwasser 32, 422 - 434

Fair, G.M. (1962): Pollution abatement in the Ruhr District, J. Water Poll. Contr. Fed. 34, 749 - 766

Imhoff, K.R. (1987): Water Quality Management in the Ruhr basin - past, present and future. Proc. 24th Annual Conference Japan Sewage Works Agency Osaka, April 1987

Imhoff, K.R. (1989): Water quality management in the Ruhr area Regulated Rivers: Research and Management Vol. 4, 119 - 128 John Wiley & Sons, Ltd.

Imhoff, K.R. (1989): Balance and elimination strategies for heavy metals, phosphorus, ammonia and AOX in the Ruhr catchment. Advances in Water Pollution Control. "River Basin Management" V, 285 - 293, edited by H. Lakari, Pergamon Press, Oxford

Imhoff, K.R. (1989): Ruhr area - Water management in a heavily industrialized region, p. 100 - 104 in: Lampert & Rothaupt (*Ed.*) Limnology in the Federal Republic of Germany, SIL-Congress, Munich

Imhoff, K.R.; Koppe, P. & Dietz, F. (1980): Heavy metals in the Ruhr River and their budget in the catchment area. Progr.Wat. Tech. Vol. 12, 735 - 749

Klopp, R. & Kornatzki, K.-H. (1987): Emission und Immission von AOX im Ruhreinzugsgebiet. Z. Wasser-Abwasser-Forsch. 20, 160 - 167

Klopp, R. (1987): Gewässerschutz durch Indirekteinleitung gewerblicher Abwasser. Wasser, Luft und Betrib 9, 27 - 34

Klopp, R. (1989): Stand und Perspektiven der gewerblichen Schwermetallemission im Ruhreinzugsgebiet. Korrespondenz Abwasser 36 (9), 1035 - 1045

Kneese, A.V. (1964): The Economics of Regional Water Quality Management, John Hopkins Univ. Press, Baltimore, Md.

Koppe, P. & Jabs, W. (1987): Anwendung des Kanalspions zum Aufspüren von AOX-Emittenten.Korrespondenz Abwasser 34, 1037 - 1039

Koppe, P. & Klopp, R. (1990): Erfahrungen mit der AOX-Methode - Analytik und regionale Bilanzierung. Gewässerschutz - Wasser - Abwasser 112, 311 - 330

Koppe, P. & Stozek, A. (1990): Kommunales Abwasser, 2. Auflage Vulkan Verlag Essen

Koppe, P. (1975): Geschichte, Aufgaben und Aufbau des Chemischen und Biologischen Laboratoriums der Ruhrverbände - 50 Jahre Gewässerschutz. GWF - Wasser/Abwasser 116, (2), 83 - 87

Koppe, P. (1980): Schadstoffelimination in Abwässern vor Einleitung in eine öffentliche Abwasseranlage unter Berücksichtigung der zulässigen Gehalte im Klärschlamm. Gas- und Wasserfach GWF 59, 159 - 176

Koppe, P. (1987): Indirekteinleiterkontrolle als Instrument der Gewässerreinhaltung. Handbuch Wasserversorgungs-u. Abwassertechnik, Bd. 2, 469 - 471, Vulkan Verlag Essen

Morgenschweiss G. & Nusch E.A. (1985): Fließzeitmessungen in der Ruhr mit Hilfe von Tracerverfahren Selbstverlag Ruhrverband, Essen

APPENDIX

INTERNATIONAL REGISTER OF POTENTIALLY TOXIC CHEMICALS (IRPTC)

Joe Banerjee

The International Register of Potentially Toxic Chemicals (IRPTC) was officially set up in 1976 following up a recommendation of the 1972 United Nations Conference on the Human Environment held in Stockholm and a decision of the UNEP Governing Council in 1974. The central unit of the register, known as the Programme Activity Centre (PAC), was set up in Geneva in 1976.

One of the initial objectives of the IRPTC was to facilitate access to scientific and legal data on hazardous chemical substances considered environmentally significant. By providing access to such data on a global scale it was hoped to encourage international cooperation in determining the impact of chemicals on man and the environment. Its aims were officially revised by UNEP's Governing Council in 1989 with five main goals.

1. To make it easier to obtain the existing information on production, distribution, release, disposal and adverse effects of chemicals.

2. To identify the important gaps in our knowledge of the effects of chemicals and call attention to the need for research to fill those gaps.

3. To help identify potential hazards from chemicals and wastes and to improve awareness of the dangers.

4. To provide information about national, regional and global policies, controls and recommendations on potentially toxic chemicals.

5. To help implement policies for the exchange of information on chemicals in international trade.

IRPTC is considered an essential tool in optimizing the use of chemicals for human well-being and at the same time providing a global early warning system of undesirable environmental side effects. It's global network has had considerable impact on the flow of scientific and technical data, and regulatory information on chemicals. Central data files have been developed on many chemicals of international significance and these are in constant use for hazard assessment and risk evaluation at both national and international levels.

In order to help Governments improve chemical safety at a national level, IRPTC has a close working relationship with the International Programme on Chemical Safety and other international organizations and is involved in chemical safety related programmes run by bodies such as the EC, OECD and former CMEA. It also has contacts with national and international scientific institutions, NGOs and Industry.

IRPTC maintains a databank of centralized computer files linking a formal network of government-nominated institutions. These are called National Correspondents. One of the important functions of the IRPTC is to train National Correspondents and other personnel in the use of the register. There are currently 121 Correspondents in 112 countries and they play a pivotal role in all IRPTC activities. Correspondents are usually specialists in one or more fields such as toxicology, public and occupational health, agriculture, industrial and environmental sciences.

However, it is their close links with authoritative bodies that provide environmental protection services in their country that is of special significance to the IRPTC. These links enable them to obtain information on relevant national legislation and regulations on control of chemical hazards and reports and reviews on chemicals and on accidents and incidents resulting from the loss of chemicals into the environment. Correspondents are also well placed to access data banks and information systems in their home country relevant to the IRPTC's activities. Furthermore, they are responsible for the promotion and distribution of IRPTC publications to individuals, institutions and industries. Readers interested in contacting the National Correspondent in their country should contact the IRPTC at the address given below.

Another important activity of the IRPTC is its Query Response Service. This service has been in operation almost since the IRPTC's inception in 1976. Table 1 shows how the number of queries have grown since the 11 enquiries in the first year. It should be noted however that the number of enquiries does not reflect the number of chemicals to which the IRPTC responds to, since one query may request information on numerous chemicals.

Table 1 Queries received by IRPTC (1976-1991)

Year	Yearly total	Cumulative total
1976	11	11
1977	11	22
1978	19	41
1979	34	75
1980	46	121
1981	69	190
1982	105	295
1983	197	492
1984	201	693
1985	335	1028
1986	292	1320
1987	312	1632
1988	350	1982
1989	450	2432
1990	423	2855
1991	601	3456

Source: IRPTC

The Query-Response Service is operated free of charge as there is a concern that fees would deter queries. Furthermore, the service is of great benefit to IRPTC staff as well, as it identifies areas that are either not covered or covered poorly.

The IRPTC database is run on a mainframe computer at the International Computing Centre in Geneva. A version of the entire database is available on-line in Canada through Health and Welfare Canada in Ottawa. The Legal File and the Waste Management File may be accessed on-line through ECDIN, the Environmental Chemicals Data and Information Network of the EEC at the host DIMDI in Cologne, Germany.

Even with its own computerized database on chemicals, other sources are also often consulted, when necessary, to answer questions. Once again its links with organizations help in the speedy procurement of information.

IRPTC is currently in the process of converting its database to operate on a personal computer such that the data are even more readily available. At the outset a limited number of network and contributing partners, restricted to national authorities and associated institutes, will receive the data and the software during the first phase of the release in 1992. A wider scale distribution is envisaged at a later date.

IRPTC publishes the Legal File (covering over 8,000 chemicals) and the Waste File of the Register as independent documents. Both are currently being updated with an aim to produce them early in 1993.

The IRPTC Bulletin is the official journal of the International Register of Potentially Toxic Chemicals and is devoted to information on hazardous chemicals. It is published twice a year and although the subscription price is US$25 per annum, preferential rates are available particularly to interested parties in developing countries.

In 1983 a project was begun to help developing countries establish national registers of potentially toxic chemicals (NRPTCs). IRPTC worked with five countries in 1984 and a further five in 1986. The countries are Brazil, China, Colombia, Gambia, Indonesia, Malaysia, Sri Lanka, Tanzania, Thailand and Zambia.

In addition to setting five main goals in 1989, UNEP's Governing Council also provided special provisions known as the Prior Informed Consent (PIC) procedure as part of the London Guidelines for the Exchange of Information on Chemicals in International Trade. PIC is the principle that a chemical banned or severely restricted for health or environmental reasons should not be shipped in international trade without the agreement of the importing country. A procedure was provided for countries to record their decisions on such chemicals in a formal way.

Under the procedure countries are provided with Decision Guidance Documents, designed to help them to assess the PIC chemical's health and environmental risks, in order that an informed decision (on whether they wish to ban or allow future import of the chemicals concerned) can be made. It is then up to participating countries to enforce these decisions. Details of these exchanges are entered into a joint PIC FAO/UNEP database. The procedure was initiated in the autumn of 1991, with the distribution of Decision Guidance Documents for the first six pesticides.

Initially, the procedure will be applied to chemicals banned or severely restricted in ten or more countries. Furthermore, some acutely hazardous pesticides found to be causing problems under conditions of use in developing countries will be included, even though they have not been banned or severely restricted in any country. Eventually the procedure will be applied to all chemicals banned or severely restricted in any country.

IRPTC was established primarily to aid national authorities responsible for the protection of human health and the environment, but its services are available to everyone. Readers interested in obtaining a more thorough understanding of the works of the IRPTC should direct their enquiries to the following:

The Director,
IRPTC/UNEP,
Palais des Nations,
CH - 1211 Geneva 10,
Switzerland.

Tel: 41-22-798-8400
41-22-798-5850
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