GUIDELINES OF LAKE MANAGEMENT

Volume 5

MANAGEMENT OF LAKE ACIDIFICATION

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International Lake Environment Committee
United Nation Environment Programme

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FOREWORD

Acidification is a serious problem for many lakes in the Northern Europe and Eastern North America. There are, however, clear indications that the problem of lake acidification also may become a problem in many developing countries in the coming decades. Southern China, for instance seems to be the next region which will suffer from acidification of lakes caused by acid precipitation.

It is important that the developing countries learn from the mistakes of the industrialized countries. The experience shows that it is always more cost effective to solve pollution problems at an early stage of their development; the longer the pollutants have accumulated in the environment, the more difficult and expensive the pollution abatement will be. It is better to use early warnings and to try to prevent the pollution problem, than to try to solve it after the environmental degradation has occurred. It is therefore important for the developing countries to learn about acidification of lakes, and to understand the reactions of lake ecosystems to acid precipitation. This will enable the developing countries to react rapidly at the first signs of acidification, and avoid the catastrophes we have experienced in some lakes in the industrialized world.

This Guideline book number five on Acidification explains in detail the relations between sources, i.e., air pollution caused by sulfur and nitrogen oxides, and their effects on lakes. Management possibilities and strategies against acidification are discussed. Indeed, an early use of such environmental management initiatives should be considered to avoid changes in the structure of lake ecosystems, which would otherwise make lake restoration more difficult. It is my hope that the developing countries will use this information in order to be prepared to meet possible forthcoming lake acidification at an early stage, thereby avoiding the mistakes made in the industrialized world.

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Nairobi
December 1992

FOREWORD

In view of the ever-increasing importance of lakes and reservoirs as sources of freshwater supply, the physical and chemical degradation of lake and reservoir environments is now an emergent issue that needs worldwide cooperation. The survey of the state of world lakes, which has been carried out jointly by ILEC and UNEP since 1987, revealed the prevalence of six major environmental problems over the continents: 1) water level subsidence due to overuse of lake water, 2) accelerated siltation, 3) acidification 4) toxic contamination and 5) eutrophication, all of which may eventually lead to 6) the collapse of lake ecosystems with resultant losses of biodiversity and many endemic species of plants and animals. It is regretted that these problems were not explicitly emphasized in Chapter 18, Protection of the Quality and Supply of Freshwater Resources, of Agenda 21 agreed upon by the UN Conference on Environment and Development held in Rio de Janeiro five months ago.

Among these, the acidification of lake water is somewhat different from the others in that a large number of lakes in a few limited regions, such as Scandinavia and northeastern parts of North America, have been collectively damaged. This was probably caused by the geographical location of the regions in relation to industrial centers emitting huge amounts of acidic air pollutants and by the poor buffer capacity of soils that depend on geological conditions. However, other parts of the world may not be free from the danger forever. Acid precipitation itself is now prevailing over most industrialized areas and even certain less developed areas of the world. If acid rain continues to fall, the lakes in those areas may be influenced suddenly as soil buffer capacity is exhausted. Environment managers should, therefore, always be careful about the possible future acidification of the lakes for which they are responsible.

Representing ILEC's Scientific Committee, I would like to extend our special thanks for the continued support to this serial publication by UNEP and the other organizations concerned. The Committee gratitude is also due to the editor, Professor S.E.Jørgensen and other contributors to this volume.

Tatuo Kira
Chairperson, Scientific Committee of ILEC Foundation.
November 1992, Otsu

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CHAPTER 1

INTRODUCTION: OVERVIEW OF THE PROBLEM

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1.1 What causes the problem?

Acid waters are observed in areas with calcium-poor but quartz-rich soil and where acid precipitation occurs. It implies that acid waters are seen in Central Europe, Scotland, Scandinavia, Belgium, The Netherlands, a minor part of France, Canada and the Northeastern states of U. S. A, Australia, New Zealand and Japan, see Overrein et al. (1980).

Acid rain has probably been observed for centuries, although acidity was not measured until about 100 years ago. The problem has, however, increased during the last decades due to man-made emissions. Emissions of natural and anthropogenic acidic gases on a global basis are about equal, but in the more industrial Northern Hemisphere, man-made emissions account for 90% or more of total acidic emission.

In the presence of carbon dioxide at atmospheric pressure and at a temperature of $20^{O}C$, rain will have a pH of 5.6, and if we also include the presence of other natural generated gases, the background value of rain is probably about 5.0. It is therefore relevant to define acid rain as rain with a pH of less than 5.0. In industrial regions rain is, however, ten times more acidic, namely pH 4.0 and in some very polluted areas rain may be transiently even more acidic, to a pH of 3.5.

Only a minor part of the total precipitation will fall directly on the surface of lakes. The processes between the ions in the rain water and the soil are therefore significant for the over-all acidification of lakes, which will be determined by the following processes and factors: the carbon dioxide pressure in the soil, release and uptake of ions from the vegetation, dissolution of weak acids, oxidation and reduction of sulfur - and nitrogen compounds (nitrification produces hydrogen ions, while denitrification consumes hydrogen ions), accumulation and release of sulfur compounds, ion exchange processes and the retention time. The typical result will be, that ammonium-, nitrate- and hydrogen ions will be retained in the catchment area, while sodium-, chloride-, potassium- and magnesium ions will be released. Release will take place for either aluminum ions or hydrogen carbonate ions, dependent on the pH.

Table 1 shows typical observations from Norway, where acidification of lakes is considered a major problem. The results are approximate average values from SFT (1982). It is seen from the table that a significant amount of the hydrogen ions is being removed by the catchment area.

Table 1.1

Typical concentrations of rain and drainage water in areas with little buffer capacities.

Component	**Rainwater**	**Drainage water**
Water mm.	1000	700
Hydrogen ions keq/km^2	60	20
Sodium ions keq/km^2	50	100
Potassium ions keq/km^2	4	6
Calcium ions keq/km^2	10	35
Magnesium ions keq/km^2	9	20
Aluminum ions keq/km^2	-	15
Ammonium ions keq/km^2	24	low
Sulfate ions keq/km^2	40	52
Chloride ions keq/km^2	41	59
Nitrate ions keq/km^2	26	3
Cations total keq/km^2	118	118
Anions total keq/km^2	118	118

The acidity of drainage waters is therefore generally less than that of incident rains, but in some cases, however, where soils and vegetations generate acidity, such as in peat bogs or organic soils, the acidity of surface waters may exceed that of rain even by an order of magnitude, for instance in the Amazonian region, where rain is about 5.0, while pH of streams might be as low as 2.8. The removal of acidity by the catchment area is, however, not sufficient to eliminate acidification in areas with low buffer capacities.

The pH of the lake water is regulated by the hydrogen-carbonate buffer system for pH > 5.5, while the aluminum buffer system becomes active below pH 5.0. An iron buffer capacity will take over by even lower pH values (below 4.0). No

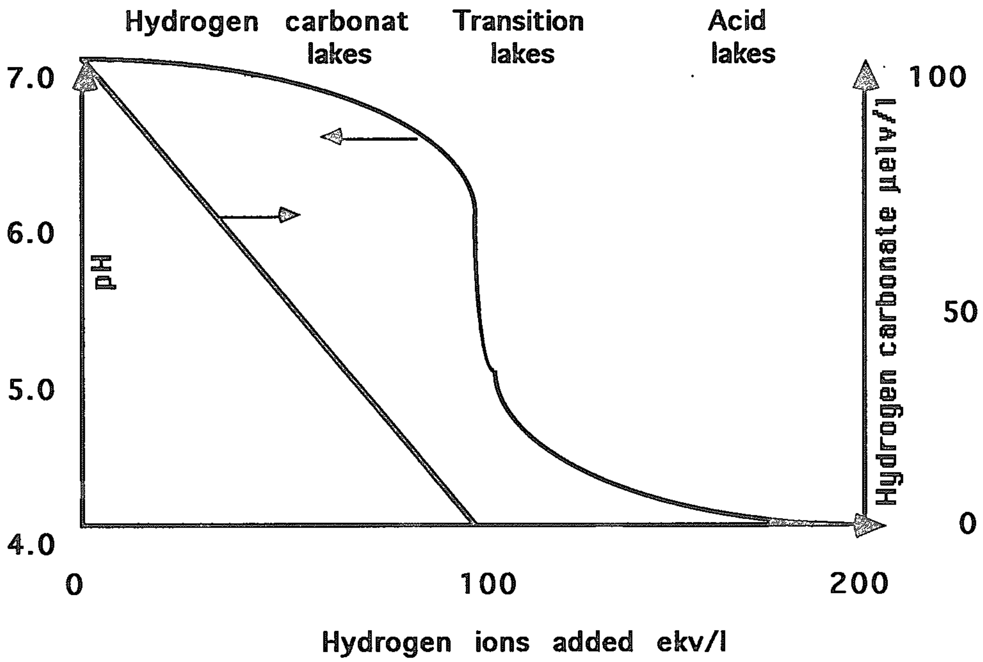

Fig. 1.1. A titration curve for lake water with 100 eq/ l hydrogen carbonate. The hydrogen carbonate buffer capacity explains that the pH is changed slowly between 7.0 and 6.0, while a rapid change will take place between 6.0 and 5.0. Below 5.0 the aluminum buffer capacity takes over. A classification of the lakes in accordance with the pH is shown. Above 6.0: hydrogen carbonate lakes, between 5.0 and 6.0: transition lakes and below 5.0: acid lakes.

biological changes will be observed, as long as the hydrogen-carbonate buffer system is active. When this buffer capacity has been used, seasonal fluctuations in pH will be observed with elevated aluminum concentrations.

The acidification process may be considered as an acid titration i large scale (Henriksen, 1980). Figure 1.1 illustrates such a titration plot for a hydrogen carbonate concentration of 100 μeq/l. Addition of 100 μeq/l hydrogen ions causes only a pH change from about 7.0 to about 6.0 due to the buffer capacity of the hydrogen carbonate system, while a further addition of only < 10 μeq/l is sufficient to provoke a pH change to 5.0. The aluminum buffer capacity becomes active below 5.0, which explains that the pH again is changed slowly.

This Guideline book focuses on the wide consequences of pH fluctuations and low pH-values on the lake ecosystem, i.e., the transition lakes and the acid lakes. Significant changes of water chemistry and in the lake ecology are observed in these lakes, which make acidification of lakes a determining pollution problem in environmental management. As an increasing number of lakes all over the world suffer from pH fluctuations and low pH values, the problem will show an increasing importance during the coming decades, unless plans for reduction of the emissions of acidic gases are launched.

1.2 Distribution and Frequency of Acid Lakes.

Extensive sampling in several regions of the world has been carried out during the last decade to identify the distribution and frequency of acid lakes.

In a survey in Northeastern U.S.A. in 1984, Linthurst et al (1986) observed that approximately 8% of the lakes could be declared acid, i.e., the pH was below 5.0.

In Canada, it is estimated that half of the 700,000 lakes in the six Eastern Provinces have alkalinity values below 50 eq/l. and thus are judged acid-sensitive. More than 7000 lakes in the Eastern Provinces have been sampled to evaluate chemical evidence for acidification. It was found that about 5% of the lakes had zero alkalinity (NAPAP, 1990).

In Sweden, of an estimated total of 85, 000 lakes, as many as 4000 lakes are classified as seriously acidified and 18, 000 lakes are reported to be acidic during some critical periods, such as snow-smelt (Monitor, 1985). A survey of the lakes in southern Norway (Henriksen et al, 1987 and 1988) shows that the highly acid waters are concentrated in the southwestern region, where pH of rain is 4.3 or less. In this area it is reported that thousands of lakes are acid and have zero alkalinity. In Finland a survey of 8000 lakes showed that 500 were acidified (Kamari, 1985).

Areas in Britain considered susceptible to acidification are western and upland areas, i.e., in northwest Wales, Cumbria and western Scotland. In these regions at least 24 major lakes are acidified - understood as $pH < 5.6$, (Battarbee et al., 1989).

Acidified lakes are reported in many other surveys, for instance in Denmark, northern Germany, the Netherlands, Austria and Switzerland. The acidified lakes are in many cases found where acidic waters drain sandy soil and afforested terrain.

Historic data for lake chemistry have been invoked to demonstrate a progressive acidification in many areas. These studies are often flawed, inevitably, by inconsistent methods of sampling and analysis. Even so there is strong evidence, that many lakes demonstrate a decline in pH over the past 100 years. As much as two pH-units are reported in several lakes. In Sweden, where thousands of lakes have been acidified, the best documented and reliable examples suggest that the pH changed from above 6.0 to below 5.0 from the 1940s to the 1970s, changing rather little since (Sanden et al., 1987).

1.3. Outlines.

This introduction to the guideline book on acidification has defined the problem, showed and explained why it is concentrated in certain regions and demonstrated the vast extent of the problem in these regions.

The following chapter focuses on the sources of the problem. Which emitted gases can cause acidification, and what is the relative importance of the various gases in relation to their acidification effects? The major parts of the acidifying gases arise from the use of fossil fuel, but the different types of fossil fuel, i.e., heavy fuel oil, gas oil, gasoline, natural gas and so on, are contributing very differently to acidification. The chapter gives an overview of these relations to be able to link acidification with the energy policy of industrialized countries.

Chapter three is the core chapter, as it deals with the effects on lake ecosystems. The effects may be classified in three groups: the effects on the chemistry of lake water, the effects on the biota of the lakes and the effects on the lakes as ecosystems. The effects on the biological components of the lakes are particularly important and are also unfortunately very pronounced. The effects on the various trophic levels: phytoplankton and macrophytes, zooplankton, planktivorous fish and carnivorous fish, are a natural classification of the biological effects.

Chapter four focuses on restoration methods. It has been widely acknowledged that environmental problems can only be solved by the use of a combination of environmental technology, alternative technology and ecotechnology. The first mentioned type of technology is covered in chapter five. The use of alternative technology implies that we, in the long run, switch to alternative energy, which does not emit acid gases, and ecotechnology implies that we attempt to solve the problems in the ecosystem once they have appeared. The chapter will present the available methods to bring the lake ecosystems back to normal - it means, in this case, to repair the damages due to acidification and to bring the pH back to above 5.0. Cases on the use of ecotechnological methods will be presented in this chapter, both successful and less successful ones.

The fifth chapter gives information on environmental models available to obtain an overview of the problems of acidification. Environmental management is increasingly using models as a synthesizing tool to compare different management strategies. It is, therefore, not surprising that a whole series of models have been developed to solve the problems related to acidification of lakes. A chain of models is available to link the source with the pH of the precipitation with the pH of soil with the pH of drainage water with the change of lake water chemistry with the biological changes in acidified lakes. The entire chain will be presented, although most details will be given for the later links of the chain as they are directly involved in lake management problems. However, the entire chain is needed to develop a proper environmental management strategy. Political decisions should ultimately be dependent on all the models in the model chain.

The fifth chapter is furthermore devoted to a brief review of the abatement methods available to reduce the emission of acid gases. The proper abatement of this pollution problem requires that we go to the roots of the problems. The models presented show how it is possible to link emissions with the effects on the lake ecosystems, while chapter five attempts to answer the crucial question: To what extent is it feasible to reduce the emissions of acidic gases with the present energy pattern? A detailed answer to this question will require a comprehensive treatment of uptodate air pollution technology, which is beyond the scope of this guideline book. This chapter can therefore only give an overview of what it is possible to obtain with the technology of today to enable the reader to understand what can be achieved in trying to solve the problem. Chapter Six and Seven are devoted to two case studies, where the detailed measurements, observations in general on the effects of acidification and the problem solving initiatives are included in the presentation. Chapter Eight is devoted to a review of the problems associated with the acid rain in Canada, where the problem is almost on the same level as in Europe.

The volume has two appendices. The first appendix presents the concepts of double logarithmic representation, which is very useful to get an overview of the relationships between pH and the chemical composition. The second appendix gives information on the global emission of acidic gases. The present problems of acid rain are concentrated in Europe and North America, but it can be foreseen, that several other regions will meet this crucial pollution problem within one or two decades.

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CHAPTER 2

SOURCES, POLLUTANTS AND ABATEMENT POSSIBILITIES

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2.1 Introduction

The history of air pollution

Air pollution is not a new phenomenon, and historical accounts and literature abound with references to the polluted air of cities. A more systematic effort to improve the conditions was first made in England in the last century, in particular with the introduction of the socalled "Alkali Act" in 1863 directed against industrial pollution. But it was not until after the Second World War that - inspired by severe pollution episodes - it was recognized that industrialization could cause unacceptable deterioration of our environment and our living conditions. In England an episode in 1952 in which 4000 people died, led in 1956 to the "Clean Air Act".

Most important is the use of fossil fuels for energy production. But there are other contributory factors notably industry and agriculture. All these activities give rise to the emission of a series of compounds, such as sulfur dioxide, nitrogen oxides, organic compounds, carbon monoxide, carbon dioxide and heavy metals. Most of these compounds are found in nature and are also emitted in natural processes e.g. volcanic eruptions and biological decay. It was, therefore, for many years believed that air pollution problems could be solved by an efficient dispersion of the pollutants, so that they could be assimilated within the natural cycles. As a result of this procedure, many urban problems were solved, but the problems soon grew to a larger, regional scale, comprising areas the size of Europe and North America.

Neither is such transboundary air pollution, which acts on a larger scale and inter alia leads to acidification of soil and freshwater, something new (Cowling, 1982). Systematic investigations of the chemistry of precipitation were not performed before the beginning of the 1950s, and the first quantitative analyses of the transport mechanisms were made around 1970, but the effects had been observed a century earlier.

The final extension of air pollution appears to be on a global scale. Already now we have observed a significant increase in the concentrations of the trace gases, which determine the global heat balance and thus the climate. In the next century we may observe the effects in the form of increased temperatures and rising sea level (Warrick, Barrow, Wigley, 1990). Of concern is also the depletion of the ozone layer in the stratosphere, which protects us from excessive solar UV-radiation.

Along with the geographical extension of air pollution, new problems arise on a local scale due to new products or new industrial processes. It also appears that air pollution may lead to pollution of soil and water through deposition of pollutants or, if the flue gas is rinsed, by leakage from deposits of residual matter.

A chain of events and decisions

Irrespective of the compounds and the scale in space and time, the problems concerning air pollution can be regarded as a chain with several links (Figure 2.1). It starts with a technical/socio-economic choice, e.g. to produce electricity by burning coal. It has the complication that coal contains sulfur, which is oxidized to sulfur dioxide and released into the atmosphere. Here it is dispersed and simultaneously, partly or fully, transformed to sulphate. Finally it is deposited and has some unwanted effects, e.g. acidification of lakes. Some pollutants act directly in the atmosphere (carbon dioxide and greenhouse effect), other may first pass through a food chain (heavy metals and damage to human health).

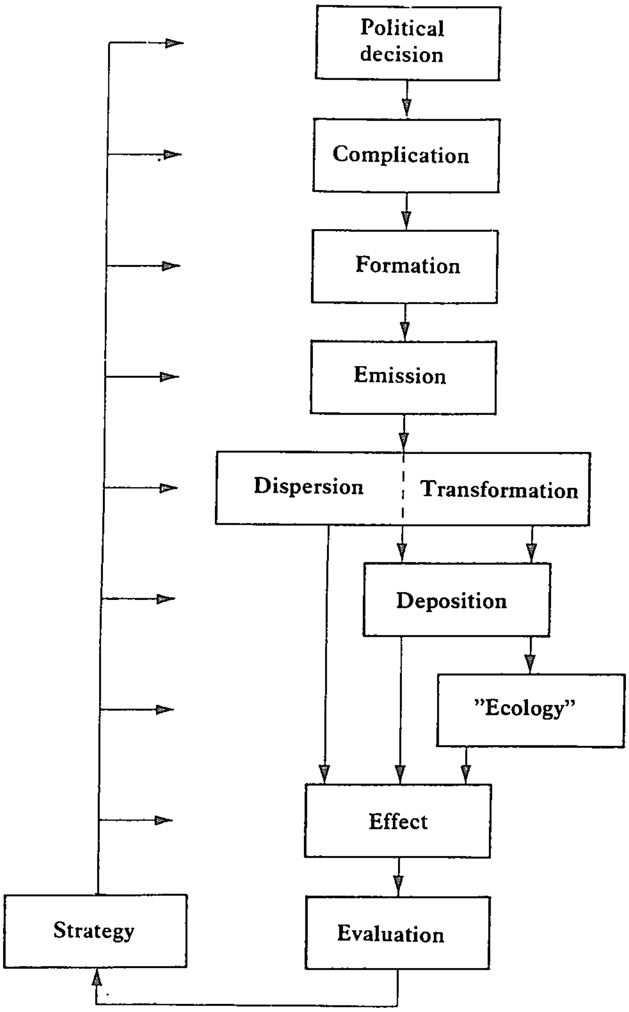

Fig. 2.1 Air polution can be regarded as a chain of events. An abatement strategy can in principle be set in at any link.

An abatement strategy can in principle be launched at any link: choice of other means of production (nuclear, wind or solar power), cleaning of flue gas or release through high stacks to facilitate dispersion. It is also possible to reduce - or compensate for - the effects, e.g., by avoiding contaminated food, using resistant materials or liming acidified lakes.

Most of the possible strategies cause environmental stress; in the energy sector e.g. there is the risk of contamination of ground water from deposits of waste products and the visual impact and noise from windmills. These stresses should all be taken into account in the choice of strategy and weighed against the effects of air pollution. Therefore the most effective environmental protection is attained by a reduction of the initial activity, in our example the production and use of electricity.

The content of this chapter

The present book treats the problems connected with acidification of lakes and this chapter is devoted to sources. However, all pollutants are mixed up in the atmosphere, where they interact before they have an impact on the environment. Therefore, practically all sources play a role; but the most important are those connected with energy production and energy use.

Section 4.2 describes the development in global population and energy and energy consumption, which is the underlying reason for all pollution problems. Section 4.3 and 4.4 lists the various sources and section the individual compounds of relevance to acidification. Some of them (primary pollutants) are emitted directly; other (secondary pollutants) are formed in the atmosphere during dispersion; the results of these processes are described in section 4.5. Finally to put the various emissions into perspective some regional and global effects are briefly rewieved. The conclusion is that, although direct acidification processes are mainly related to emission of sulfur- and nitrogen oxides, a series of other pollutants play a role via various processes in the atmosphere.

2.2 Global Development

The world population has by and large increased exponentially from an estimated 10 millions 10,000 years ago to now about 5 billion. In the calculations performed by the IPCC (Intergovernmental Panel on Climate Change) it is assumed that the future development will result in a doubling to 10 billion around the year 2070. The largest relative growth will take place in the developing countries. For the period 1975-2000 the expected growth is 17% for industrialized countries and 70% in developing countries.

The total energy consumption in the world has increased concurrent with the population and the standard of living - in the last century by more than a factor of 10 (Figure 2.2). World wars and economic crises have only given a short slow down. The development since 1950 is shown in Figure 2.3. The consumption of all fuels have increased; however, relatively most for gas and the nonfossil energy sources: biomass, wind power, nuclear power and geothermal energy. Therefore, the emissions of air pollutants, including carbon dioxide, have increased less than energy consumption.

In 1986 the global energy consumption was 322,833 PJ or as an average 65.7 GJ per capita. There were, however, large variations from more than 400 GJ p.c. in rich, industrialized countries like Canada to 22 and 11 in China and India, respectively. The annual growth was about 2%. It is interesting to compare the ratio between emission of carbondioxide and energy production. Poland and the (former) DDR topped th list with 94 and 90 ton CO_2/TJ, China had 84, but France with a substantial proportion of nuclear power was down at 44. For Norway with a large proportion of hydropower it was as low as 21 ton CO_2/TJ.

2.3 Sources and Pollutants

The dominating sources of air pollution are all connected with the use of fossil fuel for energy production. The situation is complicated; many sources emit more or less similar mixtures of so-called primary pollutants and they have similar environmental effects. But, further, they react in the atmosphere and form new, secondary pollutants. Both in these reactions and in the effects the pollutants interact with

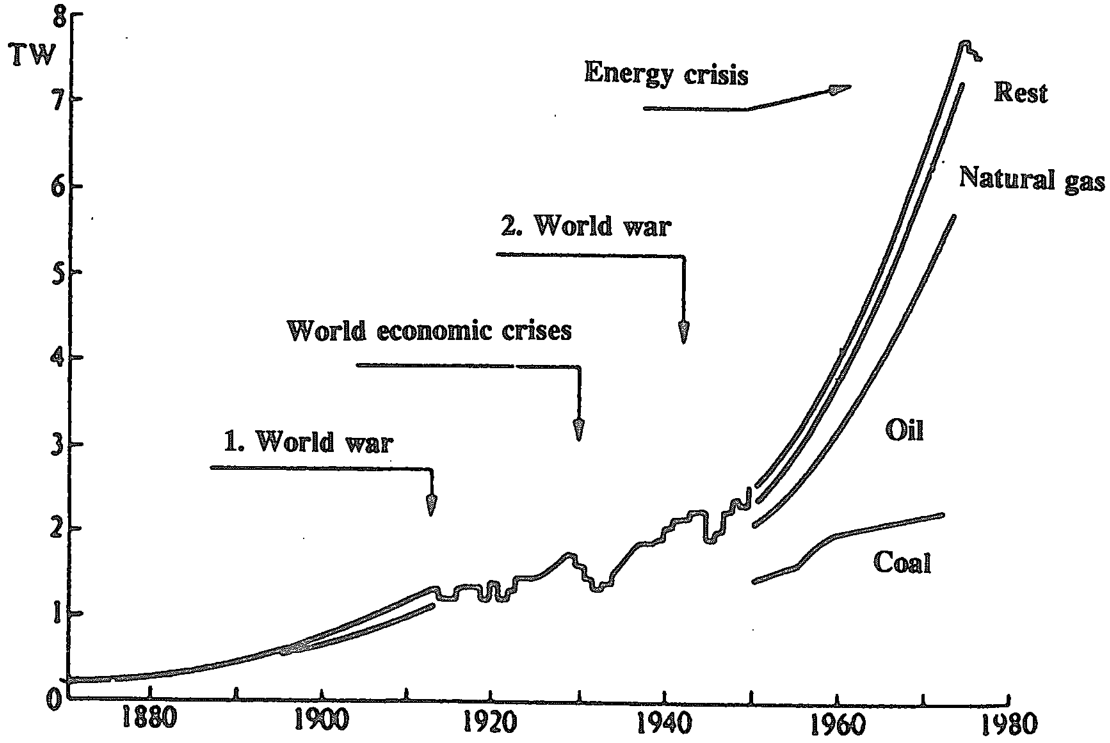

Fig. 2.2 The global primary energy consumption from the industrial revolution to the energy crises in 1973. Unit: TW=10^{12}W.

pollutants from other sources notably industry, waste inceneration and agriculture - and with compounds emitted in natural processes: volcanic eruptions, decay of organic material etc. (NSEBP, 1982-90).

Combustion processes in general

All the combustion processes, which gives rise to air pollution, are in principle oxidation with atmospheric oxygen at high temperature. In practice the oxidation takes place in a chamber - e.g. a furnace, a boiler or a cylinder in a motor. At various points in the

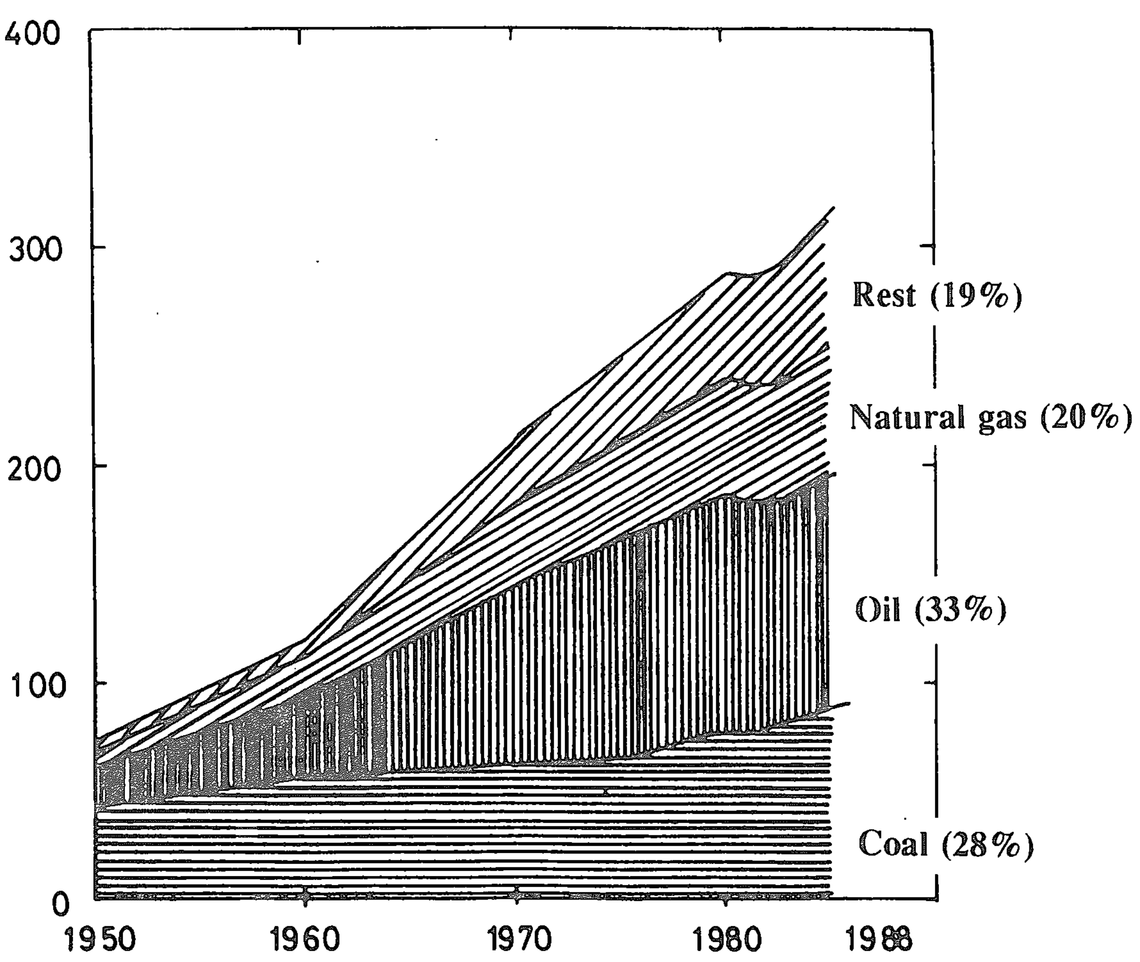

Fig. 2.3 Global energy consumption since 1950 distributed on fuels. Unit: 1000 PJ per year. "Rest" comprises all non-fossil fuels, which are converted to fossil fuel by division with an efficiency of 0.3. (Based on UN-statistics).

chamber with different temperatures and oxygen concentrations a series of reactions form a whole spectrum of compounds. Some of these are end-products (water and carbondioxide) or due to incomplete combustion (carbon monoxide and some hydrocarbons). Some are due to impurities in the fuel (sulfur dioxide, heavy metals) and some are formed during the combustion; of these the most important are the nitrogenoxides NO and NO_2, formed by oxidation of nitrogen in the combustion air. The yield of, and ratio between, NO and NO_2 depend upon inter alia the combustion temperature. The main part is normally emitted as NO, which is subsequently oxidized in the atmosphere for NO_2 (see section 4.5). Because of the tight relation between NO and NO_2, they are often added in calculations as NO_x; their emissions are often expressed in terms of NO_2.

Sulfur dioxide

The classical pollution is sulfur dioxide. By and large the sulfur content of fuel decreases with decreasing size of the fuel molecules. Thus coal and heavy fuel oil have a large content of sulfur, gas oil less, petrol very little, and natural gas practically nothing. The main sources are therefore power plants using coal and heavy oils, followed by some types of district heating, whereas the contribution from petrol driven cars and domestic heating with natural gas is insignificant. The gross energy consumption of coal and oil in Europe, and thus the emission of sulfur dioxide, was fairly constant in the first half of the century, but then nearly doubled up to the seventies. In 1985 the so-called "sulfur protocol" under the UNECE was adopted. It commits the ratifying governements to reduce national emissions of sulfur compounds by at least 30% compared to 1980-emissions before 1993.

Recent years have therefore seen a general reduction in emissions, due to an increasingly tighter regulation of the sulfur content of fuels, a shift from oil and coal to sulfur-free energy sources (such as natural gas and nuclear energy) and increasing use of flue gas cleaning (OECD, 1989).

By 1993, the total sulfur emissions of Eastern and Western Europe are expected to be 20 percent lower than in 1980, but with considerable differences between the individual countries. So far France and the western part of Germany for example, have reduced their emissions by about 55%, Denmark by about 35%, the European part of the former Soviet Union by about 15%, and Poland not at all!

In evaluating the potential for future reductions it should be taken into account that the present energy consumption in the European countries varies greatly. Expressed in tons oil equivalents pro capita the European average is about 3.3. In the (former) DDR it is nearly 6, but in France below 3. Notwithstanding different energy demands due to national infrastructure, it is obvious that there are unexploited possibilities for more efficient energy use.

Nitrogen oxides

An equally important type of pollution is nitrogen oxide. It is - as described - formed in all types of combustion, but in contrast to sulfur dioxide, the transport sector contributes significantly (in Denmark about 1/3). NO_x emissions can be reduced by modifications of the combustion process in power plants (low NO_xburners) and in cars with catalytic converters. So far however, NO_x emissions have not shown a clear trend (OECD, 1989), but in 1988 an international agreement was reached limiting nitrogen oxide emissions, in the shape of the "NO_x Protocol" under the UNECE Convention on Long-Range Transboundary Air Pollution. According to the protocol, signed by 27 countries, 1994 emissions must not exceed 1987 levels. However, some countries have expressed the intention of cutting their emissions by 30 percent before 1998. Since increasing traffic is a major source of NO_x, this goal may be difficult to obtain without strict regulations.

Ammonia

In recent years it has been realized that ammonia, emitted mainly in connection with natural and artificial fertilizers in agriculture, can be a source of nitrogen pollution of the same order of magnitude as nitrogen oxides. Depending on the desired level of environmental protection, it may be necessary to reduce these emissions in addition to NO_x emissions (Bartnicki, Alcamo, 1989).

Volatile organic compounds

Volatile organic compounds (VOC) are an important group of pollutants, which also come from natural sources, predominantly coniferous forests. Among antropogenic sources, road traffic accounts for about half of all emissions; the rest comes mainly from various industrial and domestic applications. So far European emissions have generally been increasing, but the introduction of catalysts on cars and the use of recovery systems in industry will probably change the trend.

Globally, natural emissions of hydrocarbons are much larger than antropogenic with about $2000 \cdot 10^9$kg methane and $175\text{-}440 \cdot 10^9$kg other non methane hydrocarbons (NMHC) per year.

CFCs and related compounds

A special group of organic compounds of purely antropogenic origin is the chloroflourocarbons (CFC or freons) and related compounds like the halons. They have various industrial applications such as aerosol propellants or in the production of plastic foams, where their chemical stability is exploited. In absolute terms their emissions are very small compared to other pollutants, but they are very efficient greenhouse gases and have a great potential for ozone depletion (se section 4.7). One of the reasons being their stability and consequently long lifetime. The use of CFCs is currently being phased out.

Carbon monoxide

Carbon monoxide (CO) is formed by incomplete combustion with cars as a dominating source. The introduction of catalytic converters will therefore significantly reduce the emissions.

Carbon dioxide

Carbon dioxide (CO_2) is not an "ordinary" pollutant like sulfur dioxide. It is the end product in the combustion of carbon and thus directly linked to the production of energy from fossil fuels. Therefore it is produced in such large quantities that controlled deposition is hardly technically feasible - and in any case probably only for large power plants (Laurmann, 1989; OECD, 1991).

The obvious ways of reducing CO_2 emission are therefore a lowering of the energy consumption and suitable choices of energy production. The composition of the fuel is an important factor; thus for a given amount of energy produced oil emits about 50% less carbon dioxide than coal - and natural gas only about half (see section 4.4). Various technical options offer even greater possibilities of CO_2 reduction (Figure 2.4).

All these compounds are so called primary pollutants, as they are emitted directly. Other, secondary pollutants are formed in the atmosphere.

2.4 Emission Factors and Emission Inventories

It is possible to measure the emission of air pollutants from individual sources and it is also done in some specific cases - e.g. with larger industrial or power plants, or in scientific investigations. Normally however, it is not feasible. Instead the emissions are determined from the consumptions of raw material or fuels, which are multiplied by so-called emission factors; they depend not only on the material or fuel used, but also on the process and thus on the technical installations. Table 2.1 shows some examples of emission factors for the application of various fuels in Denmark. Note that:

- These are average values (which may be different for other countries) since no fuels are pure chemical compounds. Thus coal typically only contains 80% carbon and natural gas only 91% (as volume) methane; oil products are normally mixtures of numerous hydrocarbons.
- The lighter the fuel is, the less sulfur it contains, and consequently the SO_2 emission factor is low. It is practically 0 for natural gas.
- The same tendency is seen for the CO_2 emission, but this is due to the increasing relative content of hydrogen.
- The CO_2 emissions from waste and straw are high, but since the carbon is biologically recirculated, it is of no importance.
- The emission of NO_x is stronly dependent upon the application of the fuel. For natural gas in power plants, the emission is low by direct combustion in furnaces, but high in turbines and motors - roughly corresponding to petrol in cars.

2.5 Dispersion and Transformation

As described in section 4.4 the total emission of a specific pollutant - e.g. SO_2 - can be calculated for a certain region - e.g. a country. Such results are used in international negotiations on emission reductions, but often they do not give sufficient information on the amount of damage caused by the pollution. Also the dispersion and eventual transformation in the atmosphere play an important role; consequently information with a better spatial - and sometimes also temporal - resolution is necessary.

Urban pollution

The fate of pollutants in the atmosphere depends upon various factors: the release hight, the immediate surroundings, the wind height, precipitation, and of course the physical and chemical properties of the compounds (Graedel, Crutzen, 1989).

When a pollutant is released from a "low source", e.g. a car or a domestic heating system, the immediate concentration is high (Figure 2.5) and a fraction (maybe 20%) is deposited in the near surroundings, but the major part is normally mixed within the so called "mixing layer" and transported independent of the original release height. Therefore car exhaust may both determine the local pollution level and contribute significantly to long-range transport. "High sources", e.g., power plants, on the other hand, have relatively small local effects (that is the reason for building high stacks!).

Regional pollution

Compounds with an atmospheric lifetime of only a few days can be transported several thousand kilometers with the wind and constitute the so-called "transboundary air pollution", which e.g., means that heavy metals can be found in the arctic regions. However, on a regional scale the most important factor is pollution with sulfur - and nitrogen compounds, which gives rise to acidification. Further, emissions of volatile organic compounds, which react with inter alia nitrogen oxides to form photochemical oxidants must be considered.

As mentioned, some pollution is deposited near the sources, but the smaller a country is - the more it will be influenced by its neighbours. In Europe even a fairly large country like the united Germany can only control something in the order of half of its pollution. In this situation both the scientific investigations and the abatement of air pollution must be carried out for large regions.

In Europe transboundary air pollution is studied under the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe - generally known as EMEP. It was started in 1977, and the measuring system now

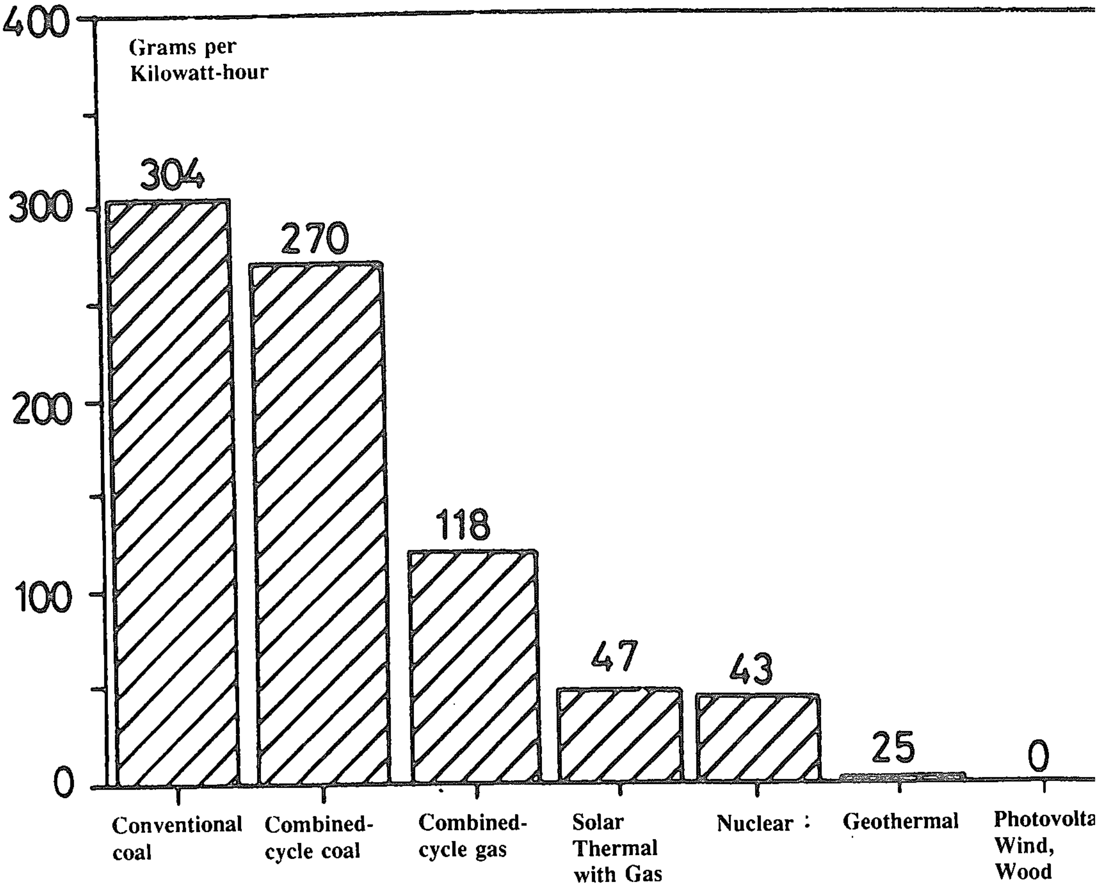

Fig. 2.4 Emission of carbon (in the form of carbon dioxide) in various types of energy production (After *Flavin*, 1989).

comprises more than 90 stations in some 25 countries. At first only sulfur was measured, recently nitrogen oxides and ammonia were included, and last hydrocarbons and photochemical oxidants are being included (Iversen et.al., 1991).

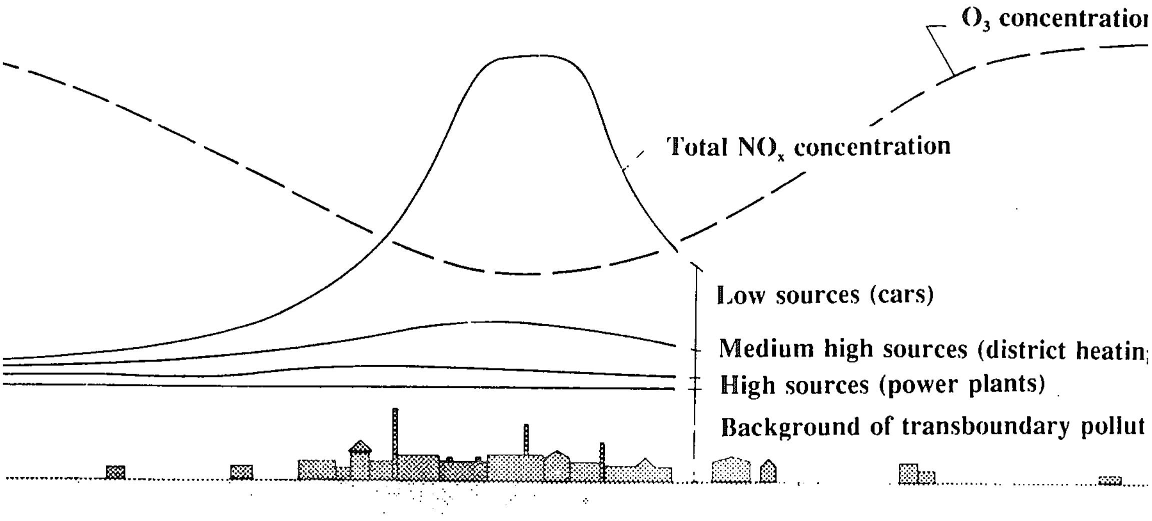

Fig. 2.5 The concentration of nitrogen oxides (NO_x=NO+NO_2) in a city with surrounding rural areas. The level is high in the city with dominating contributions from low sources - typically cars - and much lower in the rural areas, where transboundary pollution dominates. The concentration of ozone (O_3), which is reduced by NO, has a minimum effect in the city.

Model calculations are based on emission inventories, meteorological data and mathematical models for dispersion, transformation and deposition of the pollutants. All results are calculated and plotted in a 150 by 150 kilometer grid covering the whole continent. Although this resolution does not permit a detailed evaluation of the pollution effects (and offers no information whatsoever about pollution levels in urban areas) it allows a general view of the "pollution im- and exports" in Europe. It can further form the background for more detailed national calculations (e.g. Langeweg, 1989). A special presentation is applied in the RAINS model (Regional Acidification INformation and Simulation), (Alcamo et al., 1987). It allows investigations of the economy and the effects of various abatement strategies, and it can be coupled with submodels for effects like acidification and direct forest impacts.

The situation for sulfur is illustrated in Figures 2.6 and 2.7. Emissions are largest in a belt stretching from the industrial areas in England over The Netherlands, Belgium and the Ruhr District to the eastern part of Germany and Poland. And the emissions are low in the outer parts of Europe - especially in the northern part of Scandinavia. To some extent this pattern is repeated in the deposition, but it is strongly modified by the dispersion in the atmosphere and thus by the wind pattern. In Europe (Troen, Petersen, 1989) it is influenced by three major factors: the large temperature difference between the polar air in the North and the subtropical air in the South; the distribution of land and sea with the Atlantic Ocean to the West, Asia to the East and the Mediterranean Sea and Africa to the South; and finally the barriers constituted by mountain systems like the Alps, the Pyrenées and the Scandinavian chain.

North of about 40°N (i.e. in most of Europe) the wind regime consists mainly of eastward moving weather systems. Therefore pollution is predominantly transported from the West to the East; consequently e.g., the U.K. is much less polluted with sulfur than corresponding to its emissions, Denmark "imports" some pollution, but "exports" more, whereas the opposite holds for Sweden.

The pattern for nitrogenoxides is roughly the same as for sulfur; only the emissions in eastern Europe are relatively smaller due to less car-traffic. Ammonia and ammonium salts have a relatively short lifetime and consequently also a short range.

Photochemical air pollution

Among transformations in the atmosphere the formation of photochemical oxidants is of special interest. Several hundred coupled reactions between nitrogen oxides and hydrocarbons form, under the influence of sunlight, inter alia ozone (O_3). Whereas the ozone formation in the classical Los Angeles smog is an urban phenomenon, it is in Europe largely a regional phenomenon. The potential for photochemical ozone and long range transport in Europe has been calculated (Derwent, 1990) to be between 240 and 320 $\mu g/m^3$, which is in good agreement with observations during most photochemical episodes. However, in major source regions, such as Europe's industrial areas, sometimes much higher concentrations are observed. These peak values presumably are due to local scale ozone production during specific meteorological conditions.

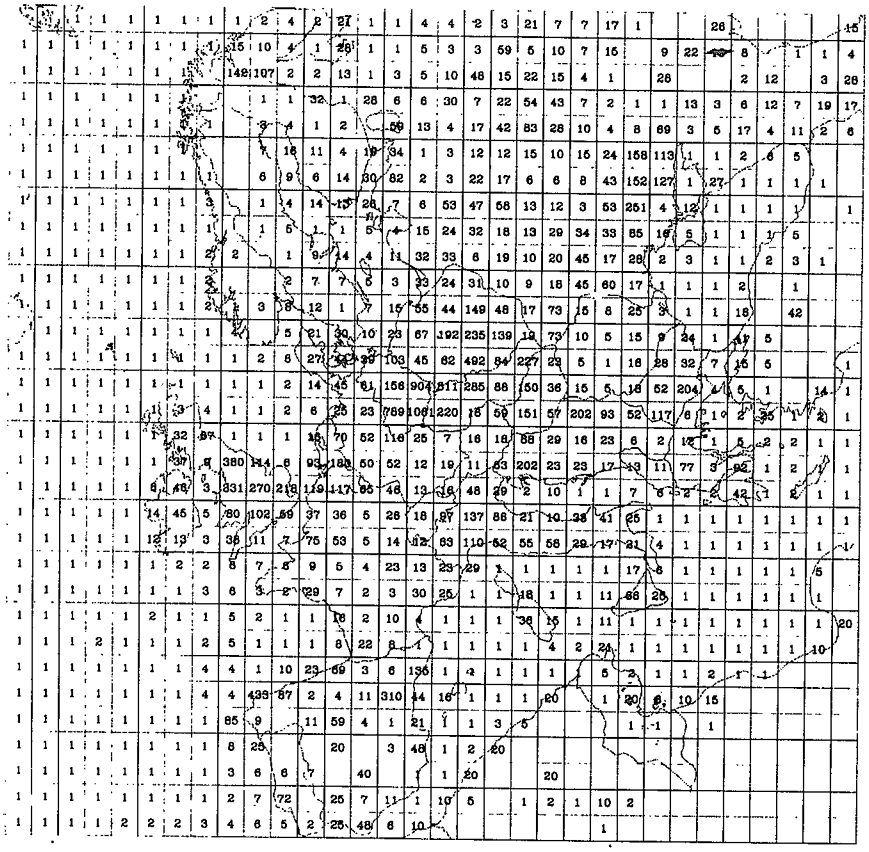

Fig. 2.6 European emissions of sulfur dioxide in 1989. Unit 1000 t sulfur per 150 x 150 km (22,500 km^2)(*Zlatev,A.*, personal communication).

The concentration of ozone is strongly related to the nitrogenoxides. In the troposphere, and under the influence of sunlight, ozone is formed by:

$$NO_2 \xrightarrow{h\gamma} NO + O$$

$$O + O_2 \rightarrow O_3$$

On the other hand ozone is reduced by NO, which is the dominant nitrogen oxide in e.g. car exhaust:

$$NO + O_3 \rightarrow NO_2 + O_2$$

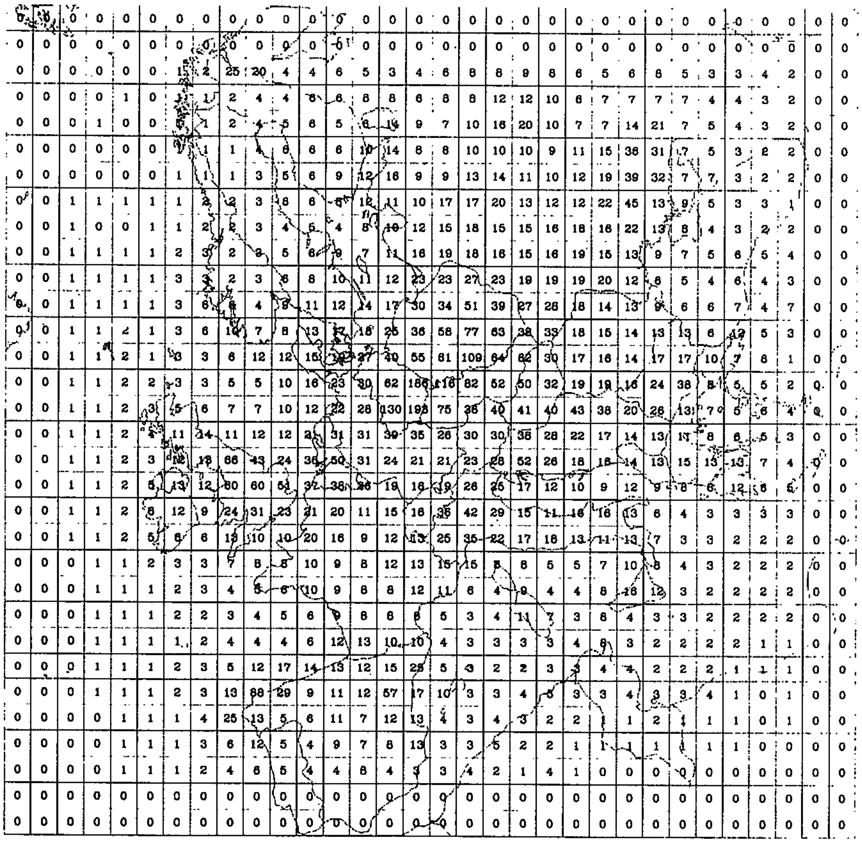

Fig. 2.7 European sulfur deposition in 1989. Unit: 100 mg sulfur per m^3 (*Zlatev, Z.*, personal communication).

Therefore ozone concentrations are often relatively low in cities - and especially during pollution episodes.

The oxidants have harmful effects in themselves, but also play an important role in the oxidation of primary sulfur- and nitrogen oxides to sulphate and nitrate and are thus part of the acidification processes. However, abatement of ozone pollution is more complicated than for e.g. SO_2, since it is not emitted directly. If the levels should be reduced to below published air quality criteria guidelines or critical levels, both national emissions of nitrogen oxides and hydrocarbons should be reduced by 50-90%. However, even after the Luxembourg Agreement for reductions of exhaust emissions from motor vehicles a substantial potential for exceeding the guidelines exists, one reason being that peak values are more important than average values for ozone.

2.6 Regional Problems - acidification and forest decline

Air pollution with sulphates and nitrates, which may be transported over distances up to thousands of kilometers, leads to a general acidification of precipitation. Unpolluted rain has a pH of 5-6, but in Europe typical values are about 4.5, and occasionally values down to 3 have been registered (Hanssen et al; 1990).

In many areas, especially in the northern part of Europe, precipitation is larger than evaporation from the surface. Therefore water will percolate through the soil to groundwater, waterstreams and lakes. In soils with a large content of lime (calcium carbonate) the acidification can be neutralized by release of calcium ions, but in other cases the pH in the soil water will drop. This leads to dissolution of a series of metals like aluminium, manganese and iron. Aluminium compounds can be especially toxic for tree roots and for the fauna in lakes and waterstreams. In fresh water, damage will start at pH less than 6.5 and all normal animal life will be gone at pH below 5 (e.g. A-nianson, 1982).

On the other hand, sulfur and nitrogen compounds are also fertilizers, and it has been argued that in some areas, e.g. in the USA, desulfurization in power plants may make it necessary to supply the fields with sulfur. It is possibly that the waste products can be used!

In areas, where nitrogen is a growth limiting factor, pollution can for a period result in increased biomass production e.g. in forests. In the long run, however, it is a dubious advantage because it may lead to deficiency in other nutrients. Then the growth will again decrease, and the surplus nitrate leach out.

It is generally known that vegetation can be damaged or killed by air pollution. In larger industrial areas and around large point sources such effects have been observed for more than 300 years (Cowling, 1982). In Europe it is most pronounced in the Eastern part, where the use of brown coal gives rise to high levels of sulfur dioxide. Further, of course, natural phenomena as drought, pests, flooding and general change in climate can influence the health and growth of plants.

In the early eighties however, an apparently new phenomenon appeared. This novel forest decline (in German: Neuartige Waldschäden) first attacked silver fir in the mountain regions of Southern Germany - generally considered a clean-air region. The symptoms were premature yellowing and loss of previous years' foliage, leading to retarded growth and ultimately death. Later the symptoms appeared on other coniferous trees and were also spred to deciduous trees and other European regions.

In 1985 it was estimated (United Nations, 1989) that in ten European countries about 24% of the total forest area was effected and 0.6% dying or dead. In a recent CEC report (European Community, 1989) it is concluded that the vitality of the forests within the region is significantly reduced since 1980 and that air pollution forms part of a complex of biotic, abiotic and anthropogenic factors. In 1987 and 1988, however, a slight improvement has been observed - especially for deciduous trees.

Soil acidification has been offered as a main cause e.g. via deterioration of the roots of the trees because of an increase of the aluminium concentration in the soil water. Against this is the fact that forest decline has also been observed on soils rich in calcium carbonate and thus having a high buffer capacity.

Another theory is that ozone, which is formed in large scale phenomena acts directly as a growth inhibitior. A special aspect is that it may decompose the protective wax layer on the needles, whereby acid rain can leach nutrients out.

Critical loads and target loads

Obviously, the harmful effects of pollution depend not only on the levels of pollution, but also on the properties of the exposed system. This has led to the concept of "critical load", which is mostly applied to ecosystems, and is defined as the highest level of deposition or concentration for which no harmful effects occur. Another concept is the "target load", which is the accepted pollution level; it may be lower or higher than the "critical load" depending on whether safety factors are applied or some damage is accepted. Thus the "critical load" is an inherent property, whereas the "target load" is a result of a political decision.

Many European countries within the ECE Convention on Long Range Transboundary Air Pollution are mapping critical loads. A special task force is responsible for the detailed planning and coordination of relevant activities related to direct effects of air concentrations of SO_2, NO_x and O_3 and indirect effects of long term deposition of sulfur and nitrogen compounds.

The critical load varies drastically with the soil properties, maybe within a few kilometers, thus in Sweden e.g. the critical acid deposition for forest soil ranges from below 10 keq/m^2yr to above 80 keq/m^2yr (Nilsson, Greenfelt, 1988). Compared with the present values, reductions up to 50% are required to avoid soil acidification which will cause damage to coniferous forests; but also some areas can tolerate 25% higher deposition.

Such detailed mapping is not manageable in political decision making. It is therefore attempted to establish acceptable average "target values". As a preliminary goal for the northern part of Scandinavia sulfur deposition should thus not exceed 0.5 g/m^2yr as an average for a 150x150 km^2 EMEP square. The nitrogen deposition should correspondingly be below 1 g/m^2yr. Present values are too highly by a factor of 2. In the central part of Europe, however, depositions of sulfur and nitrogen are up to 10 and 5 times, respectively, too high. In other words, full protection of natural ecosystems calls for a 90% reduction in emissions of sulfur dioxide. For nitrogen dioxide, which is also a prerequisite for formation of photochemical oxidants, a 75% reduction is necessary.

It is then an important question to what extent effects of pollution can be reversed. Disintegrated historical monuments can of course be restored and protected against further decay, but the authenticity will be lost. Liming of acidified lakes can restore pH to normal values, but continuing liming is necessary. Thus in Sweden some 25% of the acidified lake area has been successfully treated. There is, however, consensus (Barth, 1987) that the only lasting solution is a reduction in deposition, and observations and model work suggest that then recovery is possible within one decade.

Air pollution and sea pollution

Most air pollution sources are land-based, but some, not yet fully accounted for, contributions come from ships and various off shore activities. But also air pollution from land-based sources is deposited on sea surfaces, predominantly of course in areas near the coasts and in inner waters. In Scandinavia there is a special interest in the supply of nutrients, notably nitrogen compounds, which in first instance lead to algal bloom, and in the second - when they die and decompose - may result in oxygen deficit and a consequent death of bottom fauna (Nordic Council, 1989).

In the Baltic Sea direct airborne nitrogen deposition accounts for roughly 40% of the total load and airborne phosphorus load for 10%. In the North Sea about 25% of the nitrogen pollution is airborne. In addition to this, it must be assumed that an unknown fraction of run-off from rivers originate from pollution deposited on land. It is therefore not unreasonable to assume that nearly half of the pollution leading to eutrophication is due to emissions to the atmosphere.

Since the coastal zones serve as breeding grounds for many species of fish, also pollution with heavy metals is important. In many cases airborne pollution accounts for more than 50% and is thus more important than pollution from rivers and sewage outlets.

2.7 Global Effects

Pollutants with a lifetime of months or more can be mixed up in the entire global atmosphere and may change its basic composition. This leads to two related problems: The greenhouse effect (Warrick, Barrow, Wigley, 1990; IPCC, 1991) and the depletion of the ozone layer in the stratosphere (Gribbin, 1988; Deutscher Bundestag, 1988).

The greenhouse effect

The greenhouse effect is in itself one of the conditions for life on earth. Short wave radiation from the sun passes fairly easily through the atmosphere and heats the earth. The energy is reirradiated, but at a longer wavelength, where the atmosphere is less transparent. As a consequence the earth heats up until a radiation balance is obtained, and it thereby becomes about 35°C warmer than it would have been without atmosphere.

The increase in the concentration of various trace gases enhances this effect and thus threatens to upset the global climate. The main culprit is carbon dioxide, but also methane, the chloro-fluoro-carbons (CFC), some related compounds, and nitrous oxide are important. However, many other pollutants play a role - either directly or, via chemical reactions in the atmosphere - indirectly. Tropospheric ozone e.g. is both in itself a "greenhouse gas" and a part in the reactions transforming other pollutants in the atmosphere. It is also, as stated before, a gas with harmful effects.

On the other hand, ozone formed in the stratosphere (about 20 km), is indispensable as a shield against ultraviolet radiation from the sun, and it is further a stabilizing factor for the global climate. There is convincing evidence that the CFCs besides being greenhouse gases, cause decomposition of stratospheric ozone.

In judging the importance of different emissions of greenhouse gases, one must take two factors into account: The absorption properties of the molecules and their lifetime in the atmosphere. Typically a time horizon of 100 years is chosen, because this may be the length of time necessary for significant climate changes to develop; on the other hand the world may for a longer time horizon change so much that prognoses for emissions and impacts become meaningless. Table 2.2 shows the global emissions of "greenhouse gases" and their relative contribution to the global warming.

Calculations of the expected global temperature rise are subject to large uncertainties, both in the predictions of the future pollution levels and in the climate models themselves. In the first report from the "Intergovernmental Panel on Climate Change" (IPCC, 1990) four scenarios are presented - ranging from a "business as usual" development to an "accelerated policy" with rapid shift to renewable energy and only moderate growth in the developing countries. The four scenarios lead to temperature rises between 0.3°C to 0.1°C per decade. More recent calculations which have been modified by taking the heating of oceans more detailed into account, indicate a slower heating in the first part of the next century. Later the heating speeds up and by the year 2100 the "Business-as-usual" scenario gives a temperature rise of about 2.5°C.

However, these are global averages; the effect is assumed to increase towards the poles, but calculations for specific regions are even more uncertain. Typical values for Europe may be temperature rises of about 3°C in the summer and may be more in the winter. Precipitation will increase in the northern part of Europe and thus compensate for increased evaporation; in the southern part of Europe the soil will dry out.

These climatic changes will have impacts on both agriculture and natural ecosystems. Thus results of a study undertaken by the International Institute for Applied Systems Analysis (IIASA) in Austria suggest that the major vegetation zones in Europe may shift northward by about 1100 km for an average temperature increase of 5°C and a precipitation increase of 10%. For agriculture there may be advantages in the form of a prolonged growing season, thus the area in which maize can ripen may shift from the Northern part of Germany to Mid-Scandinavia. Drawbacks may be counteracted by a suitable change in crops. For natural ecosystems and forests human intervention is more difficult, and it is questionable whether the possible change will be so slow that running adaption is possible.

If the global temperature rises, the sea level will rise too, partly because water expands with temperature, partly because polar ice and glaciers melt. There are also countereffects: warmer air can contain more water and some may be transported to the poles and deposited as snow. But the net effect will be a rise.

The predictions have become less dramatic over the years. The first reports showed maps assuming complete melt down of all ice corresponding to a sea level rise of 70 m, in which case some countries would virtually disappear. At the often quoted Villach Conference in 1985 (Bolin, et al., 1986), it was concluded that a global temperature increase of 3.5°C ± 2.0°C would give a sea level rise of 20-165 cm. Now the report from the Intergovernmental Panel on Climate Change (1990) estimates a worst case rise of 65 cm in 2100 - although with an uncertainty of a factor of 2. Still this may cause considerable problems with increased coastal erosion, pressure on dike systems and direct flooding of unprotected low lying areas. Also intrusion of saltwater may threaten the freshwater supply or sensitive ecological systems in coastal areas. In Europe a series of estuaries are at risk.

Climate changes will not only have environmental effects in themselves, but will also influence the effects of air pollutants. Thus a warmer and more humid climate will - ceteris paribus - accelerate material degradation and probably make vegetation more sensitive to direct gas effects. Further, more precipitation will enhance the leaching out of nutrients and may thus cause entrophication in water systems. Conversely, with less precipitation trees with a damaged root systems may be at higher risk. Therefore regional and global effects should be evaluated comprehensively. And acidification should be viewed in the light of possible climate changes.

Ozone depletion

As mentioned before the chloro-fluorocarbons (CFC) and some related compounds (e.g. halones) cause decomposition of the stratospheric ozone layer. The mechanisms are complex with a series of interrelated reactions; but basicly UV-radiation diroclates CFC to give free chlorine atoms, which react with ozone:

$$Cl + O_3 \rightarrow Cl\,O + O_2$$

In subsequent reactions chlorine atoms are reformed and may replate the sequence. One of the reasons for the effects of the CFCs is their long lifetime (of the order of several years) in the lower atmosphere, which allows a slow mixing up into the stratosphere. Analogous to the greenhouse gases the ozone depleting pollutants are by no means equally effective. Table 2.3 lists the so-called ODP (Ozone Depletion Potentials) relative to the most common CFC 11.

2.8 Conclusion

Pollution of the atmosphere has a series of well-documented, unwanted effects. They range from immediate, local phenomena like smell - over regional effects like acidification, which appears to develop over a short span of years - to global effects, which over a couple of centuries may totally change the living conditions on earth.

Earlier it was possible to solve many problems by effective dispersion of pollutants, which then entered the natural cycles. With the increasing world population and its demand for a reasonable standard of living this is an outdated solution. Air pollution - as well as other types of pollution - must be limited at the sources. Consequently, it is becoming increasingly obvious that environmental problems can not be solved locally and separately. In the case of air pollution there is a strong interplay between different pollutants both in their dispersion and their harmful effects on all geographical scales. Still some problems, like acidification, can be solved by a common effort within an area the size of Europe, but what we observe is more and more a general overload of the global systems. Then a discussion of individual causes and effects tends to become meaningless.

On the other hand, the pessimistic views expressed in "The Club of Rome's" project on the predicament of mankind "The Limits to Growth" (Meadows, et al., 1972) have been replaced by a concept of "sustainable development", which on a global scale will allow economic growth without depleting the natural resources.

This is the main theme in the report from the United Nations World Commission for Environment and Development "Our Common Future" (1987) - often referred to as the "Brundtland Report". The report discusses specifically the results of the present energy policy, which is the major source of air pollution with many compounds. It is recommended that the industrialized countries should halve the per capita energy comsumption within 40 years, and change production methods in order to further reduce carbon dioxide emissions. This in turn should allow an increase in per capita consumption in the developing countries of 30%.

It is unreasonable to believe that the rapidly increasing populations in the developing countries would be satisfied with such a modest growth, therefore climate changes may be unavoidable. In the industrialized countries, however, energy savings are technically possible and will, if effected, also result in a substantial reduction in regional transboundary pollution. The possibilities are discussed in many European countries. An outstanding example, which takes all environmental aspects into account, is the Dutch national environmental survey 1985-2010 "Concern for Tomorrow" (Langeweg, 1989).

Even if such plans were generally carried out, there would be no guarantee that all ecological systems were fully protected. But one can hope for a more reasonable compromise between the needs of modern technological society and the ensuing load on the environment.

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CHAPTER 3

EFFECTS OF LAKE ACIDIFICATION

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3.1 Overview and Concepts

Acid-base reactions are of great environmental interest, because almost all processes in the environment are dependent on pH. A few illustrative examples of particular interest for lakes are included in the following list:

1. Ammonia is toxic to fish and the ratio ammonium to ammonia is known to be dependent on pH.
2. Carbon dioxide is toxic to fish and the ratio hydrogen carbonate 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 the range 6-8. It implies that algae growth, microbiological decomposition, nitrification and denitrification are 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 very little solubility product, which implies that most heavy metal ions are precipitated at pH 7.5 or above.

It is, therefore, understandable that assessments, computations or predictions of pH and the buffer capacities are important elements in many models in limnology and environmental chemistry.

The buffer capacity ß is defined as:

$$ß = dC/ dpH, \qquad (3.1)$$

where C is the amount of acid or base in eq./l added to the water. pH and ß are often found by use of an additional computation. It is here recommendable to apply the double logarithmic representation of proteolytic species, because this method is easy to use even for rather complex acid-base systems. This approach is presented in Appendix 1.

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 (e.g., 0.1 M), boiling off the carbon dioxide formed and titrating back to a pH of 6. During this process all the carbonate and hydrogen carbonate 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) corresponds to the alkalinity, Al, and the following equation is valid:

$$Al = C_{H2BO3-} + 2C_{CO32-} + C_{BO3-} + (C_{OH-} - C_{H+}), \qquad (3.2)$$

where C = the concentration in moles per liter 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, 1981).

This chapter is concerned with the effect of low pH caused by the natural occurrence of acids for instance humic acid or by acid rain due to anthropogenic emissions of acid gases. It has already been mentioned in chapter one, that the occurrence of low pH in lake water due to acid rain coincides in far the most cases with susceptible lake ecosystems, i.e., they have a naturally low buffer capacity.

The following sections concerned with various types of effects due to low pH, are organized hierarchically, i.e., that the sequence follows the trophic levels. The second section is concerned with the trophic level zero, relating to water and water chemistry. The third section deals with phytoplankton and macrophytes - the primary producers, while section four is devoted to zooplankton. Section five looks at the effects on planktivorous and carnivorous fish and section six on amphibian and riparian fauna. Section six, the final section, deals with the effects on the entire ecosystems. All the components - chemical as well as biological - mentioned in the previous sections are interrelated. The effects on fish will also have an indirect effect on zooplankton and phytoplankton and even the composition of the water. It is therefore necessary to summarize all the effects and add the indirect effects to get the effects on the entire system. This section deals, however, not only with the entire system, but also include the components not yet covered in the previous sections.

3.2 Effects on Lake Water Chemistry

A low pH implies that hydrogen carbonate is converted into free CO_2, which is toxic to fish and other animals, as respiration is controlled by the difference between CO_2- concentration in the blood and the environment.

The processes involved can be described by the following chemical equations:

$$CO_3^{2-} \xrightarrow{+H^+} HCO^{3-} \xrightarrow{+H^+} H_2O + CO_2 \qquad (3.3.)$$

Particularly low pH-values may be observed after the melting of snow, because the acid accumulated during the winter will be dissolved in the snow water and neutralization due to the contact with the soil is reduced, as the retention time of the water is short and the soil is still frozen. As water has the highest specific gravity at 3.96 ° C, the very acid water originated from melting of snow will replace the surface water, where pH will be particularly low during the spring time.

The trends observed in many North Americans and Scandinavia lakes and even in some of the larger lakes of Europe illustrate how fast the acidification process is progressing, as shown in Table 3.1.

The solubility of most metal ions increases with decreasing pH. See Figures 3.1 and 3.2. Elevated concentrations of many metal ions particularly aluminum- ,iron- and manganese ions, but also more toxic ions such as cadmium-, copper-, zinc- and mercury ions are therefore observed. The free ions are generally more toxic to aquatic organisms than complex ions. As the formations of most complex ions are

Table 3.1
Acidification of soft-water lakes in Scandinavia and North America

Region	No. of lakes	pH Early measurements	pH Recent measurements	Average change ΔpH/year
Scandinavia				
Central Norway	10	7.3 ± 0.8 (1941)	5.8 ± 0.7 (1975)	-0.05
Westcoast of Sweden	6	6.6 ± 0.2 (1933-35)	5.4 ± 0.8 (1971)	-0.03
	8	6.8 ± 0.2 (1942-49)	5.6 ± 0.9 (1971)	-0.04
West central Sweden	5	6.3 ± 0.3 (1937-48)	4.7 ± 0.2 (1973)	-0.06
South central Sweden	5	6.2 ± 0.2 (1933-48)	5.5 ± 0.7 (1973)	-0.03
Southernmost Sweden	51	6.76 ± 0.14 (1935)	6.23 ± 0.44 (1971)	-0.015
North America				
La Cloche Mtns.	7	6.3 ± 0.7 (1961)	4.9 ± 0.5 (1972-73)	-0.06
Ontario	8	5.0 ± 0.7 (1969)	4.8 ± 0.5 (1972-73)	-0.05
North of La Cloche	7	6.6 ± 0.8 (1961)	5.9 ± 0.7 (1971)	-0.07
Mtns. Ontario	19	6.7 ± 0.8 (1968)	6.4 ± 0.8 (1971)	-0.10
Adirondack Mtns.				
New York	8	6.5 ± 0.6 (1930-38)	4.8 ± 0.2 (1969-75)	-0.05

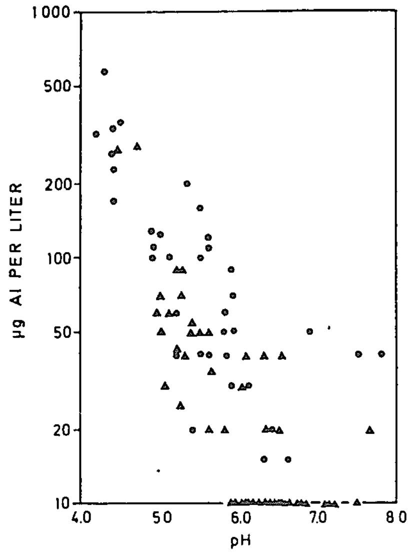

Fig. 3.1 Aluminum concentration in clear water lakes in Sweden (circles) and in Norway (triangles). Values plotted as 10μg / l are below the analytical detection limit.

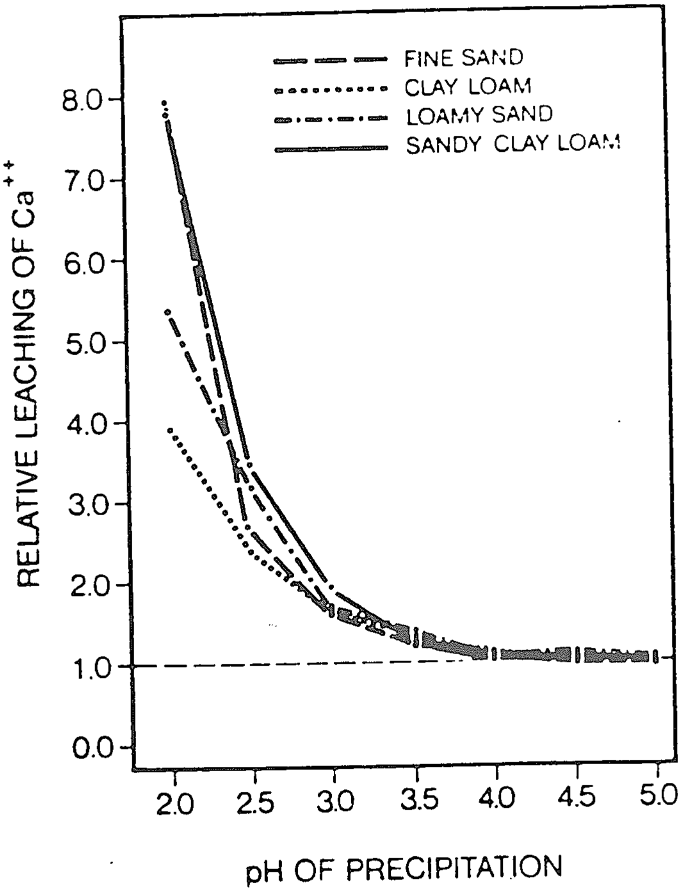

Fig. 3.2 Leaching of calcium in forest soil exposed to precipitation adjusted to pH values from 2.0 to 5.0 during a period of 40 days. The calcium leaching in the control (distilled water) is set at 1.0. Precipitation 500 mm / month.

decreasing with decreasing pH, the toxicity of most metals will furthermore increase with decreasing pH. The speciation of the metal ions are dependent on pH, as shown in Table 3.2, reproduced from Mc Donald et al. (1989).

Aluminum compounds are ubiquitous in geological and biological material. It is always in the trivalent state and forms very stable complexes with a variety of inorganic and organic material. Below pH 5.0 the form Al^{3+} increases progressively and at pH 4.0 it is the major ion present (Stumm and Morgan, 1981).

The concentration in natural fresh waters of aluminum is usually very low, in the range of a few p.p.m. Drainage waters from deforested areas or acid waters (pH < 5.0) have, however, often elevated aluminum concentrations, mainly consisting of Al^{3+} or complexes with hydroxides, fluoride or sulfate.

Table 3.2

Major species of metal ions as function of pH

Metal	**pH 7.5**	**pH 5.0**	**pH 4.0**
Aluminum	$Al(OH)_4^-$	$AlOH^{2+}$, $Al(OH)_2^+$	Al^{3+}
Cadmium	Cd^{2+}, $CdOH^+$	Cd^{2+}	Cd^{2+}
Copper	Cu^{2+}, $CuCO_3$	Cu^{2+}	Cu^{2+}
Iron	$Fe(OH)_2^+$,$Fe(OH)_4^-$	$Fe(OH)_2^+$	$Fe(OH)_2^+$
Lead	$PbCO_3$,$PbOH^+$	Pb^{2+}	Pb^{2+}
Manganese	Mn^{2+}	Mn^{2+}	Mn^{2+}
Nickel	Ni^{2+}	Ni^{2+}	Ni^{2+}
Zinc	Zn^{2+}, $ZnOH^+$	Zn^{2+}	Zn^{2+}

Debate continues as to which aluminum species are toxic. There is some evidence from laboratory studies that $Al(OH)^{2+}$ at pH between 5.0 and 6.0 is the most toxic component for fish (Sadler and Lynam, 1987), while $Al(OH)_4^-$ has been correlated with toxicity to algae (Helliwell et al., 1983).

Increased accumulation of mercury and cadmium is observed in acidic lakes (Johansson, 1980). Mercury is found in the form of methyl mercury ions in acid lakes, while mercury in neutral and alkaline lakes is found as dimethyl mercury. The latter has a higher vapor pressure and has therefore a smaller retention time in fresh waters than the methyl mercury ions, which in addition is more easily bioaccumulated in fish.

Henriksen and Wright (1978) have examined the concentrations of the series of heavy metal ions (Zn, Pb, Cu, Cd) in Norwegian lakes and found that the acidic lakes generally have higher concentrations. It has not been stated whether the higher concentrations are due to direct deposition or drainage waters.

3.3 Effects on Primary Producers

pH increases generally with eutrophication due to uptake of hydrogen carbonate ions by photosynthesis, see Fig. 3.3, which demonstrates the seasonal variations in a hypereutrophic lake. Long-term reductions of pH may force lakes into an increasingly more oligotrophic state, as suggested by Grahn et al. (1974). See Fig. 3.4. The explanation is that either carbon may be removed as carbon dioxide at pH below 5.0 and carbon therefore becomes the limiting nutrient, or that phosphate is reduced due to precipitation by the elevated concentrations of aluminum- and iron ions by lower pH. The allocation of diatoms is found to be highly dependent on pH. Five well-defined groups are used in this relation:

acidobiontic, occurring at pH < 7.0, maximal at pH < 5.5.
acidophilic, occur at pH < 7.0
indifferent, occur equally at circum neutral pH
alkaliphilic, occur at pH > 7.0
alkali biontic occur at pH > 7.0

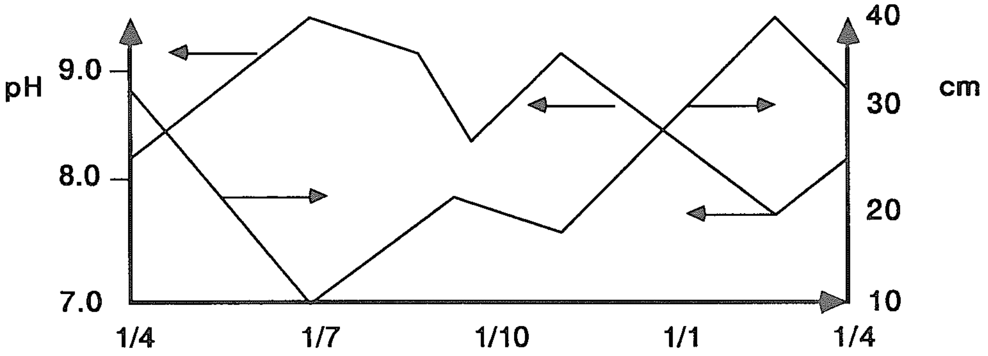

Fig. 3.3 The seasonal variation in transparency (cm) and pH in a hypereutro- phic lake, Lake Glumsoe, Denmark.

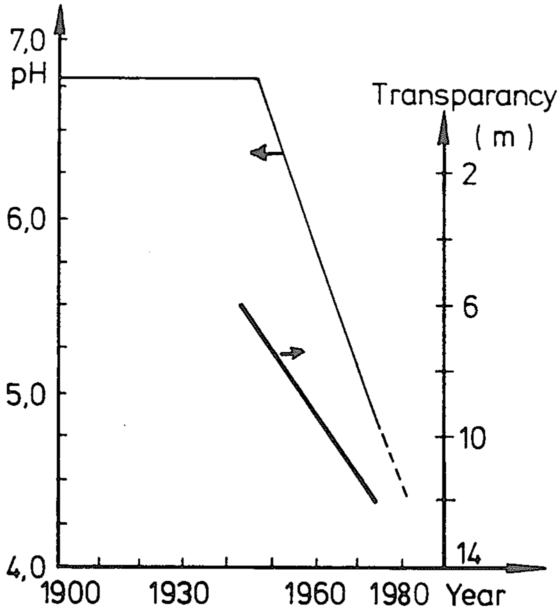

Fig. 3.4 pH and transparency of Lake Stora Skarsjön plotted versus time.

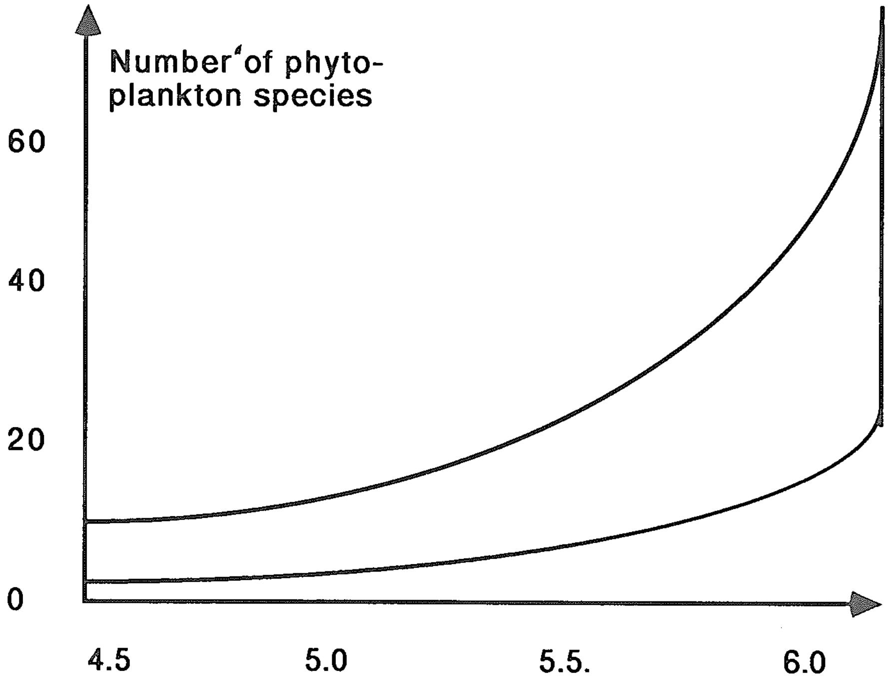

Fig. 3.5. The number of phytoplankton species observed in Swedish lakes versus pH of the lake water according to Johansson and Nyberg (1981).

It is possible to state the approximate pH (by +/- 0.25 units) by determination of the relative occurrence of the five groups. This relationship has been used extensively to reconstruct pH history from sediment core (Howells, 1982).

A decreased pH implies a reduction in the number of phytoplankton species present in the lake. Fewer and fewer species are adapted to the acidity, as pH decreases. Fig. 3.5 shows the number of observed species in Swedish lakes plotted versus pH (Johansson and Nyberg, 1981).

An early manifestation of acidification in Swedish waters was the abundance of underwater *Sphagnum* moss in lakes of pH below 5.0, where it replaced *Lobelia-Isoetes* communities, which is characteristic for oligotrophic lakes at pH above 5.5. This shift in the composition of the macrophyte community reinforces the acidification, as *Sphagnum* generates hydrogen ions by ion exchange with calcium ions. The diversity of macrophytes declines as does the diversity of phytoplankton with increased acidity. An examination in the English Lake District showed, that lakes with some alkalinity have about twice the number of species of acidic lakes (Stokoe, 1983).

3.4 Effects on Zooplankton and Aquatic Invertebrates

The differences between acidic and neutral lakes are mostly a replacement of species and a pronounced decrease of the species diversity; see Figure 3.6. A similar result as the one shown in Fig. 3.6 was found by Fryer and Forshaw (1979). They found a total of 68 zooplankton species in 99 low ionic strength lakes, of which the more acidic waters had only nine species.

Several studies of *Daphnia* species indicate that cladoceran species are generally sensitive to acute acid conditions. The cladoceran *Bosmina* is characteristic of acidic lakes, replacing the *Daphnia* species neutral waters. Copepods are somewhat less sensitive than cladocerans. They are usually representative of acidic waters (Brett, 1989).

Effects on zooplankton physiology are reduced filtering, hemoglobin loss, reduced oxygen and sodium uptak,e and gill tissue damage. The long term effects are reduced brood size and reproductive capacity, and delayed reproduction.

In contrast to fish, invertebrates are usually able to tolerate acid exposure of a day or two. Macro invertebrates are among the most commonly monitored groups of lakes, as they are used as "biotic" indicators of the health of lakes and streams. In lakes with moderate alkalinity and pH above 6.0, the fauna is usually rich in total species and often seasonally abundant. In lakes below 5.6, however, some taxa are absent or scarce. This is particularly noticeable in regard to may-flies, crustaceans and mollusks (Sutcliffe, 1983). Clearly some species are absent because of a specific deficiency of calcium in low alkalinity streams, such as mollusks, which require calcium for shell formation.

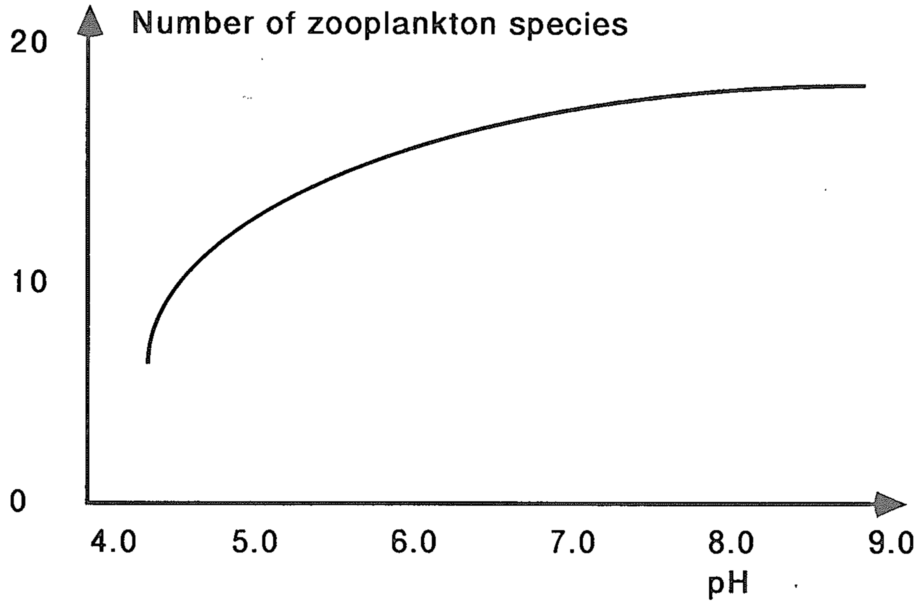

Fig. 3.6 Number of zooplankton species in Swedish Lakes according to pH. The results are from a comprehensive examination of 84 lakes in Sweden.

Some specific investigations show that the following species have poor survival below pH 5.2: *Gammarus lacustric, Gammarus pulex, Asellus aquaticus,* and *astacus astacus*; see Okland and Okland (1980), Hargeby and Petersen (1988) and Appelberg (1981).

In contrast, some insect larvae show a wide range of tolerance. It has been found that some insect larvae can survive even at pH 3.5 for long periods. Although some may-fly species are sensitive to acidity, other insect larvae (dragonfly, damsel-fly, caddis fly and stone fly larvae) are typically well represented in acidic waters.

Low acidity affects invertebrates through several toxic mechanisms, such as reduced gas exchange, impaired calcium metabolism, element deficiencies and toxic effects of aluminum ions; see Herrmann (1987).

3.5 Effects on Fish

Decreasing pH has a striking effect on the fish population, as demonstrated in Tables 3.3 -3.4. At extremely low pH values all young fish disappear completely (Almer et al. 1974, 1976 and 1978) Nevertheless, spawning and fertilized eggs have been observed even at low pH values, so it seems that the development of eggs may be disturbed by high activity of hydrogen ions in the aquatic environment. This is illustrated in Fig. 3.7, where the percentage of hatched eggs is plotted against pH value. The period from fertilization to hatching also tends to be prolonged at low pH values, as shown in Fig. 3.8. These observations are also in accordance with the trends in occurrence of fish species; see Table 3.5, which clearly shows that it is the reproduction that suffers from the low pH.

In the United States of America lakes and ponds in the Adirondacks have been studied over some decades for water quality and fishery status. A survey of fishery during the 1920s and 1930s provides a baseline for past occurrence of species. A study of 217 lakes was undertaken in the 1970s (Schofield, 1976). Of 40 sampled lakes, 21 were found to be without fish and pH was below 5.0 in all 21 lakes. A more recent study has identified a total of about 120 lakes without fish in the area. Comparison of the fishery records of the 1930s and 1975 shows that 44 lakes undoubtedly lost fish during the period. In other regions of northeast USA where acid deposition is heavy, no biological effects and no changes on Atlantic salmon resources have been detected (Haines, 1987). In Pennsylvania, where acid low-order streams are quite common, there is evidence that a few lakes have lost species.

Table 3.3

Fish status for 1679 lakes in Southern Norway grouped according to pH

pH	No. of lakes in pH range	% of lakes with no fish	% of lakes with sparse populations	% of lakes with good populations
<4.5	111	73	25	2
4.5-4.7	245	53	41	6
4.7-5.0	375	38	41	21
5.0-5.5	353	25	40	35
5.5-6.0	164	8	36	56
> 6.0	431	1	13	86

Table 3.4

Trout population and pH in 260 lakes*)

		pH							
No. of lakes	Population	4.00-4.50		4.51-5.00		5.01-5.50		≥5.51	
		No.	%	No.	%	No.	%	No.	%
33	Empty	3	9.1	17	51.5	7	21.2	6	18.2
87	Sparse population	2	2.3	15	17.2	21.2	24.1	49	56.3
82	Good population	-	-	9	11.0	14	17.1	59	72.0
58	Over-populated	-	-	3	5.2	13	22.4	42	72.3
260	total	5	1.9	44	16.9	55	21.2	156	60.0

*) Results are based on an examination carried out by Jensen and Snevik (1972).

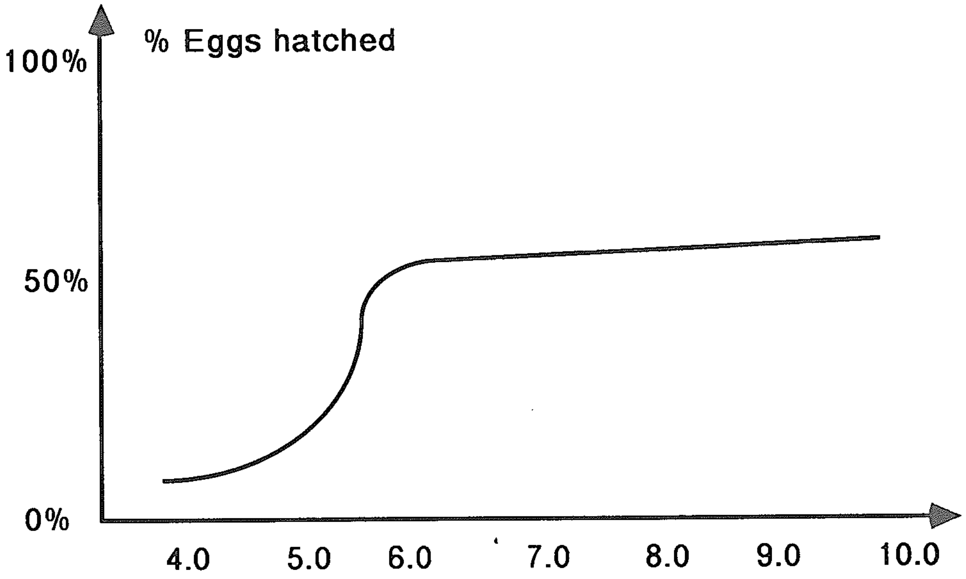

Fig. 3.7 % eggs hatched according to pH. Total number of eggs reared 253-274.

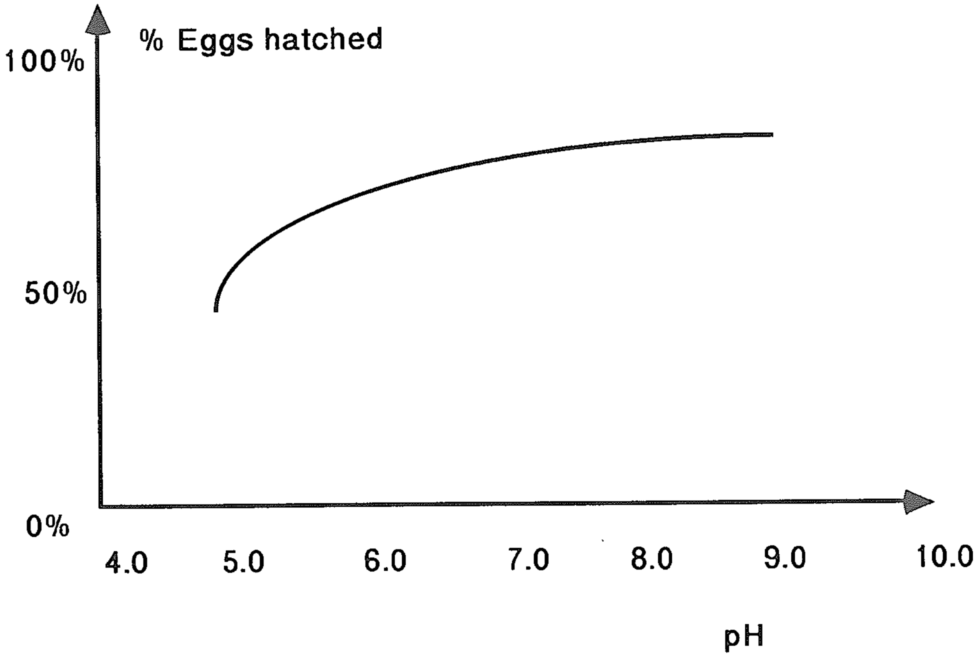

Fig. 3.8 Eggs hatched during the first 96h after fertilization as percentage of total number of hatched eggs according to pH; see Fig. 3.7.

In Ontario, about 200 lakes are considered to have lost fish populations, while filed records for nearly 3000 lakes suggest several species were relatively tolerant of low pH. The species are yellow perch, red-belly dace and pumpkin seeds. A more significant record of fishery loss is available for salmon rivers in southern Nova Scotia. In spite of low pH in several rivers and streams, the area of salmon spawning affected is estimated to be only about 10 km^2, but a much larger area is considered to be threatened.

As seen from the above mentioned results the relationship between, on the one side, the fish population and, on the other side, the pH is not completely unambiguous. Chester (1982, 1984 and 1986) suggests, that the effect on the fish population is indirect. Chester mentions the positive influence of the calcium ion concentration on the fish populations; see for instance Fig. 3.9. The figure shows that the calcium ion concentration has a strong influence on the LC-50-value of ammonia for fish. Another important indirect effect is due to the lower complexation of heavy metals by low pH, causing a higher uptake of toxic heavy metal ions by fish. This is shown in Fig. 3.10.

A characteristic of damaged fish populations in acidified lakes is, however, not just the absence of fish, but that the structure of the population is anomalous (Harvey, 1975). In a healthy population, numbers in their fist year are such that the recruitment class are usually high; most natural loss occurs during this early stage. In the following year, survival is generally good and each year class prior to migration or spawning will be represented in the population. In acidic lakes, in contrast, annual classes are sometimes entirely absent, or grossly depleted; see also Table 3.5.

Another characteristic of fish populations in acidic lakes is that there may be a few older and larger fish, possibly the remnants of populations present before the acidification.

It is clear from this discussion that water quality including acidity is considered a crucial factor in determining the success of fishery in lakes; see Table 6.

Nevertheless there are many factors to take account of and that makes the entire problem very complex.

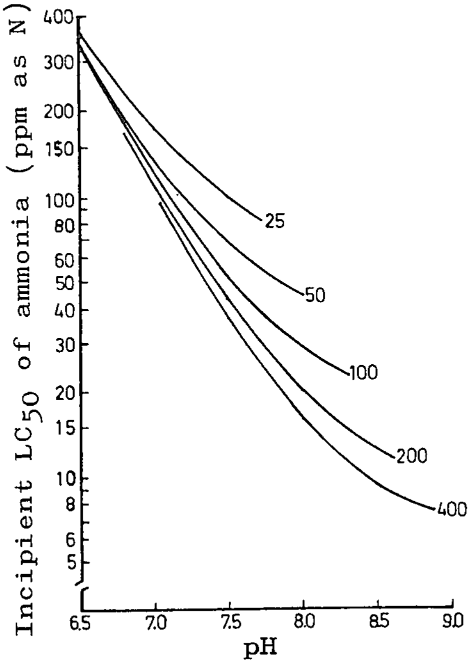

Fig. 3.9 LC-50 of ammonia for trouts versus pH at different HCO3- alkalinities.

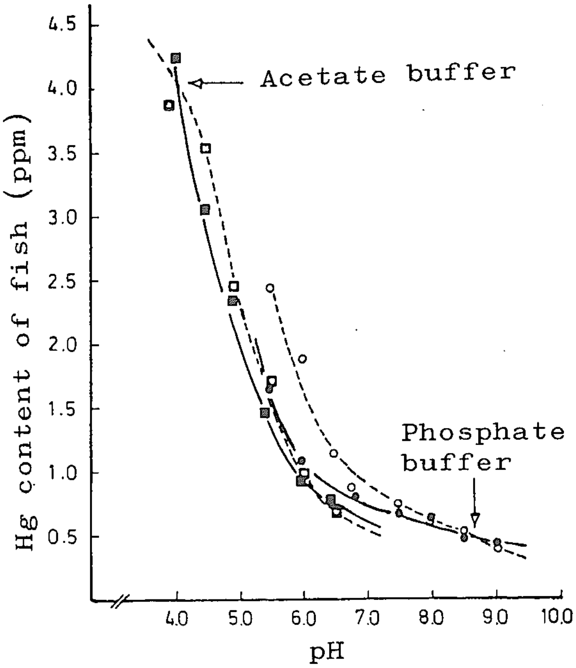

Fig. 3.10 Effect of pH on the mercury content of fish.Emerald shinner ¤; Fathead minnows ¤; Exposure to 1.5 ppm Hg from $HgCl_2$ solutions.

Table 3.5

Occurrence of fish species before acidification and species found during 1973

Lake	Earlier species forming permanent stocks	Species found 1973	Species re-producing 1973
Bredvatten	Pe Pi E	(E)	
Lysevatten	Pe Pi R E	Pe (E)	Pe
Gårdsjön	Pe Pi R T C E	Pe Pi E	Pe
Örvattnet	Pe St M	Pe	Pe
Stensjön	Pe Pi R St M	Pe Pi R	Pe Pi
Skitjärn	Pe Pi R L	Pe Pi R L	Pe Pi

Pe=perch (Perca fluviatilis, Pi=pike (Esox lucius), E=eel (Anguilla vulgaris), R=roach (Leuciscus rutilus), T=tench (Tinca tinca), C=Crucian carp (Carassius carassius), St=Brown trout (Salmo trutta), L=Lake whitefish (Coregonus albula), M=Minnow (Phoxinus phoxinus).

Table 3.6

Effects of pH values on fish (Alabaster and Lloyd, 1980)

pH-range	Effect
3.0 - 3.5	Unlikely that any fish can survive more than a few hours
3.5 - 4.0	Lethal to salmonoids. Some other fish species might survive in this range, presumably after a period of acclimation to slightly higher pH

Table 3.6 (continued)

pH-range	Effect
4.0 - 4.5	Harmful to salmonoids, bream, goldfish and carp, although the resistance to this pH increases with the size and age
4.5 - 5.0	Likely to be harmful to eggs and fry of salmonoids. Harmful also to adult salmonoids and carp at low calcium, sodium and/or chloride concentration
5.0 - 6.0	Unlikely to be harmful, unless concentration of free CO_2 is greater than 20 mg l^{-1} or the water contains freshly precipitated $Fe(OH)_3$
6.0 - 6.5	Harmless unless concentration of free CO_2 > 100 mg l-1

3.6 Effects on Amphibian and Riparian Fauna

Different species of amphibians exhibit a wide range of sensitivity to acidic water. Experimental studies have demonstrated response to acidity and particularly to the associated high aluminum levels. The common toad, *Bufo bufo,* showed some mortality in the presence of aluminum at pH 4.5 or lower. Similar results were obtained for three species frogs with a lethal pH level at about 3.5.

Effects are particularly seen at the egg hatching stage, while the larvae become progressively more tolerant and the adults of these species are found in waters of a wide range of acidity up to even pH 3.0.

Two species of salamander, *Ambystoma spp.,* showed reduced breeding success in acidic waters.

The question of ecological significance of inability to hatch amphibian species is strongly related to the pronounced seasonal nature of egg production during the spring snow-melt period, which means that hazards are high under all circumstances. However, embryos that hatch and develop to the tadpole stage are evidently resistant to acid conditions, although still highly susceptible to predators.

Riparian birds have been identified to be at risk from acidification, either directly or indirectly through other biological changes. Some species, such as dippers, are totally dependent on the adjacent aquatic ecosystem as a food source. It has been shown that dippers decline in numbers parallel to an increase in acidity in a group of streams over the past 30 years (Ormerod, 1985). In contrast, the gray wag-tail does not show this relationship, because it does not feed on aquatic insects. This led to the hypothesis that aluminum residues in the prey organisms were the cause for the reduced number (Nyholm, 1981). However, this has not been supported by analytical evidence (Otto and Svenson, 1983).

Lack of fish seems a more plausible explanation for the absence or scarcity of fish-eating birds than the aluminum concentration in fish. The reaction of some duck species illustrates the complexity of the problem. They have shown to benefit from low pH, probably due to the reduced competition from fish in acid lakes.

In line with a review by Eriksson (1983) two main factors can explain the reduced bird population at the shore line of acidic lakes: the increased concentration of toxic metal ions in the water and the reduced numbers of fish.

Concern has also been expressed regarding the effect of acidification on mammals, particularly otters. The depletion of otters seems, however, more related to the loss of habitat than to any other factors.

3.7 Effects on the Lake Ecosystem

Lakes play a significant role as a buffer on physical, chemical and biological factors in the entire catchment area.

Acidification of lakes implies a pronounced reduction in the biodiversity of the lake ecosystem. Numerous investigations have revealed a relationship between the pH of lake water and the diversity index; see for instance Likens et al. (1977 and 1979) and Okland and Okland (1980).

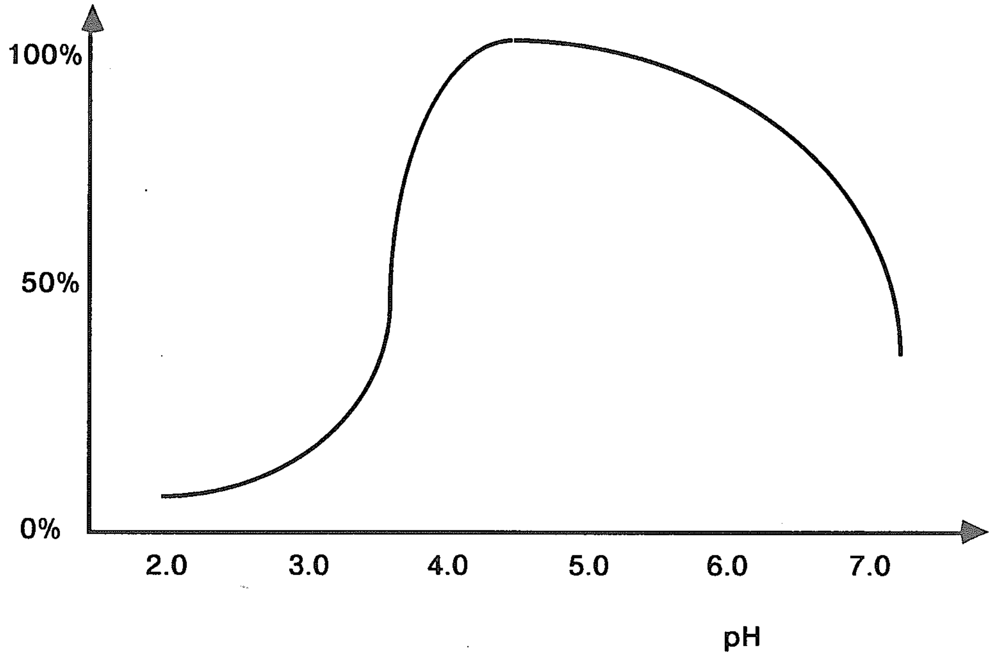

Fig. 3.11 The relative decomposition rate of cellulose plotted versus pH. The maximum decomposition rate is the pH range of 5.0 -6.0.

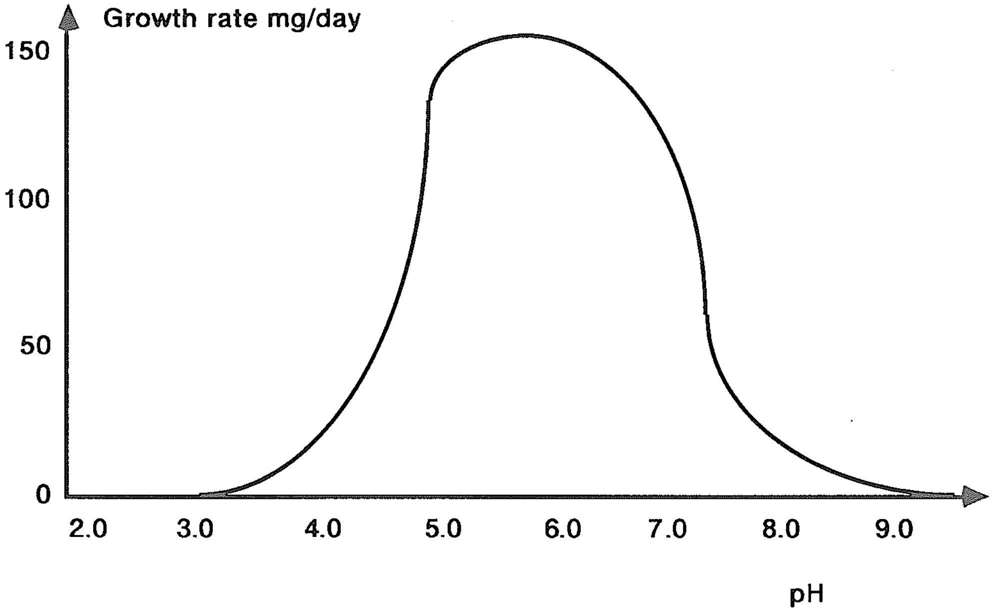

Fig. 3.12 Growth of a fungus, *Merasmius graminum,* as a function of pH.

It can be concluded that lake ecosystems become poorer in dynamics as well as in diversity - in quality as well as in quantity. It is, therefore, understandable that acidification is considered one of the most serious pollution problems in regions where acidification is a threat to aquatic ecosystems.

Another clear effect of acidification is a significantly slower turnover rate due to reduced rates of practically all biological processes. The effect is pronounced as can be seen in Figs. 3.11 and 3.12.

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CHAPTER 4

RESTORATION OF ACIDIC LAKES

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4.1 Reversibility of Acidification

There are several illustrative examples of recovery of acidified lakes. A few of these examples will be presented as basis for conclusions of the reversibility of lake acidification.

The Sudbury location is notable for its massive exposure of sulfur deposition during the uncontrolled development of metal smelters there since the end of the last century. In 1972, a major source of sulfur emission was closed and another dispersed more effectively by construction of a 381 m stack. The emissions were thereby reduced by 70%. In a lake, called Baby Lake 1 km away, pH increased from 4.0 in 1972 to more than 5.6 in 1988. Alkalinity increased and the concentrations of toxic heavy metal decreased. In a larger sample of 37 lakes in the same area, pH levels increased in all of the acidic lakes and sulfate concentrations decreased in those with highest concentrations (Keller et al., 1986).

Although these lakes suffered excessive acid deposition for almost a century their chemical recovery has been rapid, but biological recovery is delayed and the recovered communities are likely to be unstable and uncertain.

Acidification of lakes in western Sweden developed progressively through the 1940s to reach a peak in the 1970s, where pH level was about 4.5 and sulfates concentrations significantly elevated. These changes were, as mentioned in Section 3.5, accompanied by reproductive failure in fish populations. To some extent, the changes reflected hydrological conditions and in 1977 this trend was reversed and pH increased by 0.3 to 0.4 pH units. This was associated with a decrease of about 20% in the wet deposition of sulfate, but not of acidity in rain, which tended to increase, possibly due to the increase of nitrate in rain water (Forsberg et al., 1985). Recovery of water chemistry was rapid, but significant improvements in fish populations are still not recorded.

The experience gained with liming have generally given the same results as mentioned above for the Sudbury lakes and for the lakes in western Sweden. The water chemistry shows a rapid recovery, including a reduction in the concentrations of heavy metals and other trace elements, while the biological recovery is somehow slower due to hysteresis effects and slow recruitment particularly of fishes and birds. This implies that the recovery of the biological diversity is equally slow.

Technological methods used in the ecosystem or by imitation of the ecosystems (for instance the application of artificial wetlands) are often called ecotechnological methods or the application of ecological engineering; see Mitsch and Jørgensen (1989). The methods mentioned in this chapter are all ecotechnological methods, while the next chapter will deal with pollution abatement by application of environmental engineering and with environmental management by use of models. This chapter deals with in situ methods, while the regional abatement of acidification is a question of reduction of the acid gases at the source; see the overview of sources in Chapter 2.

4.2 Liming of Acidic Lakes

The acidity of lake water is determined by the concentrations of various weak acids including humic acid and hydrogen carbonate ions. The latter ions have only very small concentrations in water at low pH. Lime is widely applied to neutralize the acid ions and increase the hydrogen carbonate concentration of water. By application of lime the following processes occur:

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2O + CO_2 \qquad (4.1)$$

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \qquad (4.2)$$

Immediately after the addition of lime, pH will increase to about 8.0, but pH will afterwards be reduced to the level corresponding to the chemical reactions of the acids in the lake water and the added lime. It is desirable to achieve a pH of 6.5 - 7.0 and an alkalinity of 0.1-0.2 meq/l. It implies that about 10-25 mg of lime must be used per liter, dependent of course on the acidity of the lake water.

Other chemicals such as dolomite, calcium oxide, calcium hydroxide and sodium carbonate may also be applied, but they are usually more expensive to use. An important problem related to liming is the concentrations of heavy metals in the applied chemicals. The concentration of heavy metals in the Swedish lime corresponds to the background concentrations of heavy metals, when 10 mg lime is applied per liter in a 10 m deep lake. Typical concentrations of heavy metals in lime are: cadmium 0.2-2 ppm, nickel 10-45 ppm, mercury 0.03-0.12 ppm, chromium 6-25 ppm, copper 5-33 ppm, zinc 10-100 ppm and iron about 1%. Consequently, it is necessary to analyze heavy metals concentrations of the lime before a wide application of lake liming is initiated.

The efficiency of the liming process is dependent on the contact time and the contact surface. The distribution method for the lime in relation to its specific surface may therefore be important for the efficiency.

Liming may be performed in the lake, in the tributaries or in the entire catchment area.

Several chemical changes have been observed by liming of lakes. Usually the nitrate concentration will decrease due to increased primary production and due, to a certain extent, to increased phosphorus concentration in the lake water. Lime contains minor amounts of phosphorus, which together with the mobilization of the phosphorus in the sediment, explain the increased concentration of total phosphorus. Hultberg and Anderson (1982) find, however, a decreased concentration of phosphorus in lake water after 7 years of liming, which may be explained by a more pronounced precipitation of phosphorus by aluminum at higher pH.

Aluminium is generally precipitated by higher pH manly as hydroxide. Reductions from 500 µg/l to 100 µg/l have been observed a few months after the liming was initiated.

Due to precipitation of heavy metals, the bioaccumulations of these toxic trace metals are reduced significantly after liming. Bengtson et al., (1981) report a decline of the cadmium concentration from 0.2 µg/l to less than 0.05 µg/l after liming in Swedish lakes. The concentration in the sediment increased correspondingly, due to the precipitation.

It was emphasized in Section 4.1 that the biological recovery process is somehow slower than the chemical recovery process. Observations from several Swedish lakes have shown that even after 3-5 years of liming the loss of carnivorous fish has still not been compensated. The biological diversity was, however, increased and less acid-resistant phytoplankton species have been introduced. The benthic fauna is usually also fully recovered after a few years of liming. It may be concluded that a transition state between the biology of an acidic lake and a neutral lake was achieved, but a complete recovery was still not obtained.

It is, however, important that the microbiological activity in lakes, which have been limed for several years, has returned to the level of neutral lakes. This implies that the turnover rate also has returned to a normal level. There is still very limited experience with the long-term effect of liming, but it is possible to conclude that a complete recovery should be expected, although the time needed to obtain this is longer than previously foreseen.

Experience indicates furthermore that it is necessary to lime the entire catchment area to obtain a significant effect, although the effect of land-based liming is much slower than the effect of lime added directly to the aquatic ecosystems. Only 1-2% of the land-deposit lime is washed out per year and it is reduced after 2-3 years, see Fig. 4.1. These effects are, however, important for the long-term results of the liming, but as Fig. 4.1 further illustrates only liming of the entire or almost entire catchment area guarantees success.

The cost of liming is approximately $10-25 per ton of lime distributed. The cost is dependent on the price of the limestone, which does not, however, vary very much from place to place, and the methods of distribution. As much as 118, 000 km^2 of Sweden (= 26% of the country) needs liming, because the alkalinity of lake water is 0.1 meq/l or less. This would cost more than $20 mill. per year to carry out.

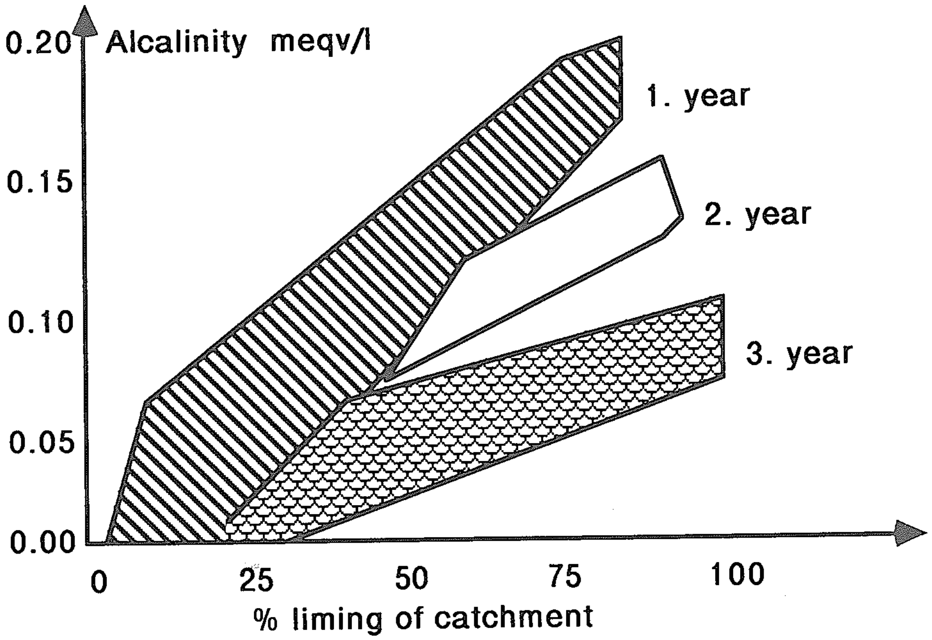

Fig 4.1 The increase in alkalinity from liming of the catchment area. The effect for the first, second and third year are shown. It is plotted versus the percentage of the catchment area limed.

4.3 The Application of other Ecotechnological Methods

Liming is the most applied ecotechnological method for reduction and neutralization of acidification. Other in situ methods may, however, be applied to obtain a higher efficiency on biological recovery. They could therefore work hand in hand with liming to obtain a faster and more complete recovery within a shorter period of time. A slower recovery due to hysteresis is known for many ecological cases, for instance eutrophication. Hysteresis is also known in context with acidification. The high hydrogen ion concentration is maintained due to production and adaptation by the species present in the acidified ecosystem. Therefore it may be important to introduce other species in addition to liming to assure the long term stability of liming. However, the application of this strategy requires that the forcing functions, i.e., the pH of the rain water, are changed. The ecosystem will otherwise return to the acidic conditions again including species composition. The forcing functions will determine the long-term conditions of the ecosystem - only by changing the forcing functions, shall we be able to recover the ecosystem, but the time needed for recovery can be changed by use of ecological engineering methods. The conclusion is therefore that we have to play on the entire spectrum of methods to obtain the best and fastest result. Liming assures a higher pH but only for a certain period (dependent mainly on the retention time of the water in the lake) if the inputs of hydrogen ions are not changed. Correspondingly, the adjustment of pH by use of liming, does change the pH, but to bring the ecosystem back to normal the application of other means is required to assure that the entire biological community is adjusted to the normal pH again.

Rohde (1981) has introduced the concept of a biological buffering system. The idea is to introduce acid-tolerant and acid-resistent algae species to increase the primary production in acidic lakes. The primary production will again raise the pH due to the photosynthesis. The method has not however been very successful up to now, as it is difficult to obtain a higher level of photosynthesis, when hydrogen carbonate ions are missing in the lake water; see Jansson et al. (1981).

The introduction of acid-tolerant fish species is another method to accelerate the biological recovery. Salmo gairdneri, the North American trout, has been proposed and applied as an acid-tolerant species with some success, particularly where liming was used simultaneously, Erikson et al., (1980 and 1987). This approach has enabled some lakes to provide satisfactory fishery due to increased fertility of the introduced fish species at the dominant pH-value of the lake water.

The application of land-use / management strategies have been explored to counter acidification, particularly that associated with growth of coniferous trees. Conifers have been replaced with broadleaf species, forest cutback, burning and ploughing regimes (Ormerod et al., 1988 and Welsh et al., 1987). The results have been an increase in pH, particularly in cases where the low pH has been caused by natural processes. If the low pH has been mainly caused by acid rain, the method has hardly any effect, at least not on a long term basis.

Hydrological management has also been used to counter acidification, where a source of less-acidic groundwater is available or increased lake retention may enhance sediment generation of alkalinity, which is the case for calcium-rich sediment.

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CHAPTER 5

MANAGEMENT AND MODELLING OF LAKE ACIDIFICATION

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5.1 Alternative Management Strategies

There appear to be no alternatives to abatement of air pollution causing acid precipitation. The ecological engineering methods presented in Chapter 4 are able to:

1) reduce the effects of lake acidification for a period of time
2) to accelerate the recovery of a lake after a significant reduction of air pollution has taken place and
3) to recover (change) lake ecosystems with natural acidity.

The use of as wide a spectrum of methods as possible is recommendable and will guarantee the biggest effects under all circumstances, but a full and stable recovery is not achieved, unless the natural or anthropogenic sources of acidic components are reduced significantly.

Chapter 2 has given a survey of the sources to acid precipitation. It will be to excessive in this context to give a comprehensive treatment on all the environmental technological methods available for reduction of acid air pollutants, as they are not related to lake ecology. Different abatement *strategies* should, however, be mentioned in this context.

Different fossil fuels have different emissions of nitrogen oxides and sulfur oxides per unit of energy produced. Generally, the emission of acid components per TJ produced increases in the following sequence: natural gas, light fuel oil, heavy fuel oil, coal (see Table 5.1). It implies that the emission of acid gases might be reduced considerably by switching, for instance, from coal to natural gas, which can be done relatively fast without huge investments. Natural gas is generally more expensive per kJ and only available in certain regions, but as abatement of pollution and recovery of damaged ecosystems often are very costly, it is necessary to calculate the *total* costs including all environmental costs to be able to make the right choice of fossil fuels. Environmental taxes have been imposed in Scandinavia to enhance the transfer from coal to natural gas with some success.

The transfer to other energy sources from the use of fossil fuel to nuclear energy or the so-called alternative energy sources will also reduce the emission of acid components. Alternative energy encompasses a wide spectrum of energy sources and may be classified in a) bio-fuel, i.e., biogas, straw and wood b) solar energy for production of hot water or electricity c) thermal energy d) wind and wave energy. All four classes are of course carbon dioxide neutral and will not add to the green house effect, but the bio-fuel will, to a smal extent, produce acidic components, although not comparable with the worst types of fossil fuel. Various types of bio-fuel are included in the survey given in Table 5.1. The shift from traditional to alternative or nuclear energy,however, requires a great deal of capital and is time consuming and takes decades to complete. It is of course possible to realize the shift step by step and each step will contribute to a partial solution of the problem. Although such a shift of energy sources will solve the problems, it is not possible in a short time to do this for a very high percentage of our energy consumption without large economic constraints.

Our modern, technological society is very dependent on energy. The consumption of energy, is not surprisingly, dominated mainly by the industrialized countries, which on average use up to 100 times more energy per capita than the poorest developing countries. Energy consumption is closely related to the gross national product and it is therefore a political issue to reduce the energy consumption, unless it of course can be done by increasing the efficiency in energy use. This is, however, possible to do by a number of means, because many uses of energy in homes and industries are inefficient. Introduction of energy tax seems to be a very effective method to increase energy efficiency and has been used in Europe and Japan, but unfortunately to a less extent in U.S., where the energy consumption per capita, even relative to GNP is disturbingly high. There seems, therefore, to be great possibilities in the utilization of this strategy to a greater extent than has been the case today, but the decision is again political.

Table 5.1.

Approximate average mission of acid components per TJ for various types of fossil fuel, calculated from average compositions.

Energy source	keq hydrogen ions per TJ
Coal	8.9
Heavy fuel oil	8.5
Light fuel oil	6.1
Gasoline	5.8
Natural gas	2.6
Biogas from organic waste	0.4
Straw	0.6
Wood	0.2

The abatement of air pollution problems by use of environmental technology has developed very significantly during the last decade or two. It is possible today to remove sulfur by desulfurization processes from fossil fuel and sulfur oxides and/or nitrogen oxides with high efficiency from smoke by a wide spectrum of technologies, but their applications are rather expensive. Consequently, they have almost excluasively been used at the major sources of acid gases, i.e., at power stations and incineration plants and only in the most advanced industrialized countries. It is in principle possible to achieve any desired reduction of acid gases by use of environmental technology. It is only a matter of investment, which will have, however, to be taken from the solution of other pressing problems. It will in other words be a matter of priority.

To summarize: we can follow three different strategies in our long term abatement of acidification and in addition to the ecotechnological methods mentioned in Chapter 4:

A. Shifts to other energy sources, which will emit less acid gases. The more sustainable environmental policy we decide to use in this direction, the longer time is required to realize the development, for instance by shift to alternative energy sources. Much more research is, however, under all circumstances needed to improve alternative energy sources sufficiently to be able to reduce costs. It is therefore important to give high priority in the short term to further research in development of alternative energy sources.

B. Increase the efficiency of energy use. Much can be achieved relatively rapidly by focusing on this strategy, but this strategy cannot alone solve the entire complex of problems.

C. Use of environmental technology either by desulfurization of fossil fuel before it is used for energy production or by removal at the major sources of acid gases. These strategies can be applied in principle immediately, but will generally require large investments.

The obvious question: "which strategy to apply?" cannot be answered simply or the answer is rather, that we should apply all three strategies simultaneously. The optimum use of all three strategies will furthermore require a good ecological-economic planning by use of environmental models, because the problem is indeed very complex. The following sections are therefore devoted to presentation of models, which attempt to compare different combinations of the three strategies - scenarios - to state the related effects on a regional basis.

5.2 The Relation between Management Strategies and Models

A series of models is needed to relate emissions of acid gases and their effects on ecosystems. Figure 5.1 shows how it is possible to couple the energy and environmental policy with the emissions of acid gases, further with the general effects on ecosystems and thereby with acidification of lakes.

Energy and environmental policy gives us information on the geographical distribution of energy consumption and the related emissions of acidic gases. The choice of energy source determines the amount of acid gases produced and the environmental legislation determines to which extent the acid gases are removed before they reach the environment, i.e., the geographical distributions of emissions are determined. It is possible in the future planning of the energy sector to "test" different scenarios, i.e., to find by use of a series of models, which effects should be expected in the future by a given plan. These results should then be used as a feedback to the energy and environmental policy. The idea is to state the optimum policy from an ecological-economic view point by this iterative method.

The energy and environmental policy information are fed into a model for the atmospheric processes of chemical and meteorological nature. The characteristic climatic data for the regions are used for this model step, as well as information on the chemical processes of the acidic gases. Precipitation data combined with the kinetics of the chemical processes in the atmosphere will provide information on the chemical composition of the rain-water. The chemical composition of the rain, the soil and the surface water will furthermore, together with the geographical information of the land-use, tell us the effects on the surface water and the soil. The effects on the soil, again, determine the chemical composition of the drainage water, which of course has an effect on the surface water. It is obvious that the entire chain of models is needed to be able to relate energy use with effects on lake acidification. The lake model encompasses all the effects in focus among all the effects mentioned in Chapter 3. It is a cumbersome modelling effort, but there is no other way to make this multi-steps relation between political decisions and the effects on the ecosystem level.

Figure 5.2 shows the grid applied for the regional model of Europe, the so-called EMEP-model (Eliassen and Saltbones, 1983, Seip et. al., 1984 and Alcamo et. al. 1990)

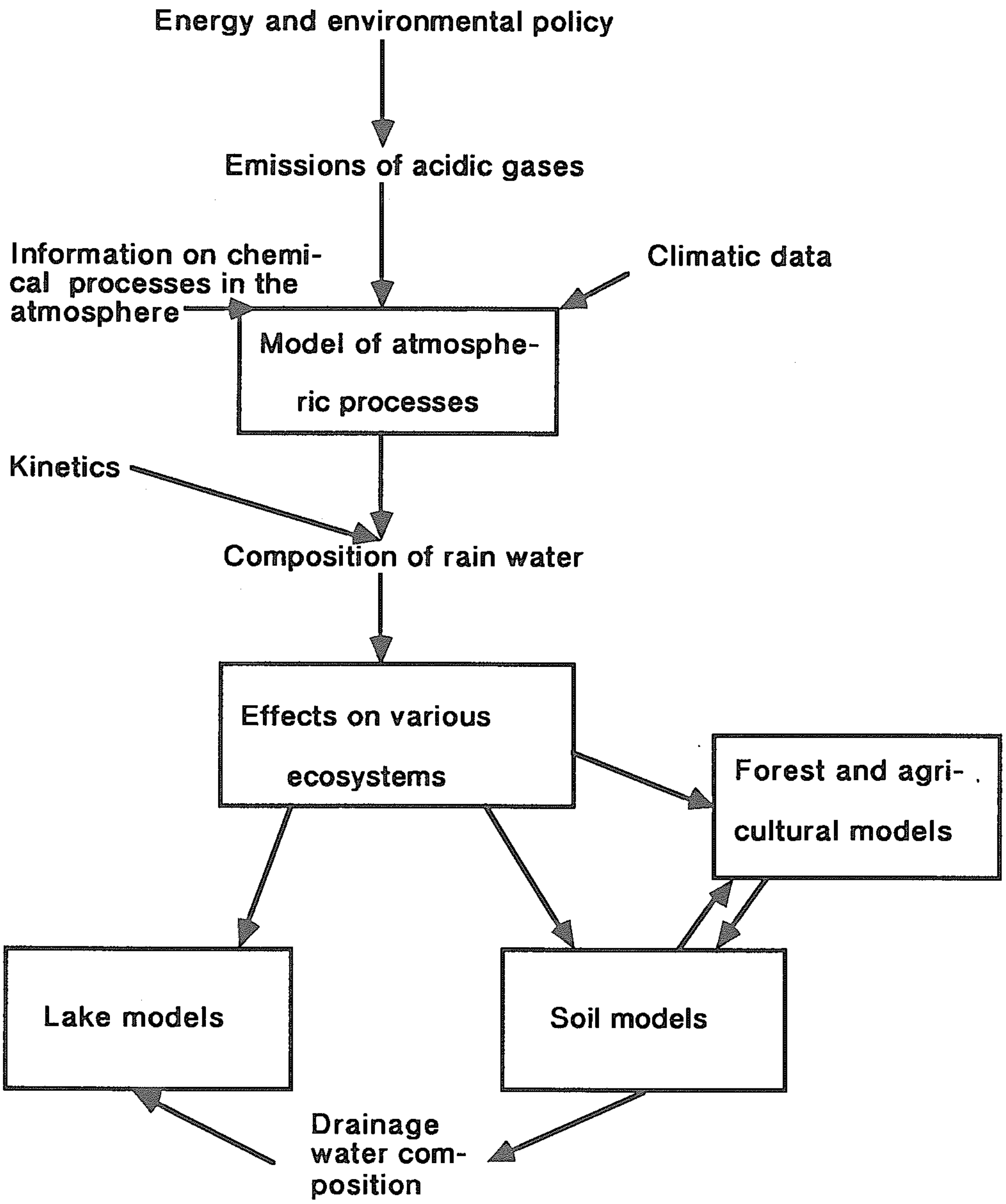

Fig. 5.1 The figure illustrates the chain of models used in environmental management to state the relationship between energy and environmental policy and the effects on lake ecosystems.

The grids are 150*150 km^2. The geographical distributions of the energy consumption and the energy sources are the starting point for the model chain and the final results are the effects on a specific lake, giving its geographical position. The meteorological data used will correspond to a characteristic year for the region. The average soil compositions are given for each grid to be able to give typical compositions of the drainage water. The effects on forest and agriculture are included in the model chain to give the feed backs between the soil and the land-use.

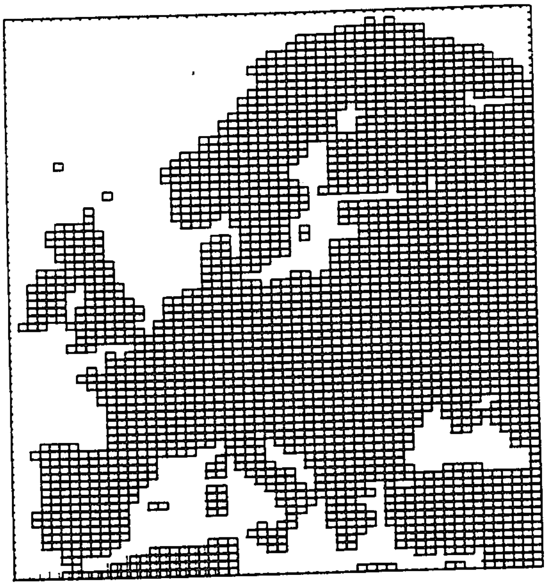

Fig. 5.2 The grid used for the European regional acidification model.

5.3 Models for Emissions and Atmospheric Processes

The Rains model (Alcamo et al., 1990) covers the entire chain of submodels, presented in Fig. 5.1. by use of the grid (or similar) shown in Fig. 5.2. The atmospheric composition is found on basis of computation of the sulfur, the nitrogen oxide and the ammonia emissions separately, as illustrated in Fig. 5.3. The first model - called energy pathways - considers the need for energy and the choice of energy sources for each 150x150 km^2 box of the grid. The economical consequences are of course included in these considerations, as the final decision always will be based upon economic-ecological consequences.

Two submodels are concerned with the control strategies of sulfur dioxide and nitrogen oxides. They give the input to the emissions of these two acidic gases. The ammonia emission is computed in parallel and is in accordance with the measured ammonia emission. It is in other words not considered to reduce the ammonia emission. It could, however, be considered in the future to include a strategy model for the ammonia emission, which mainly comes from agriculture.

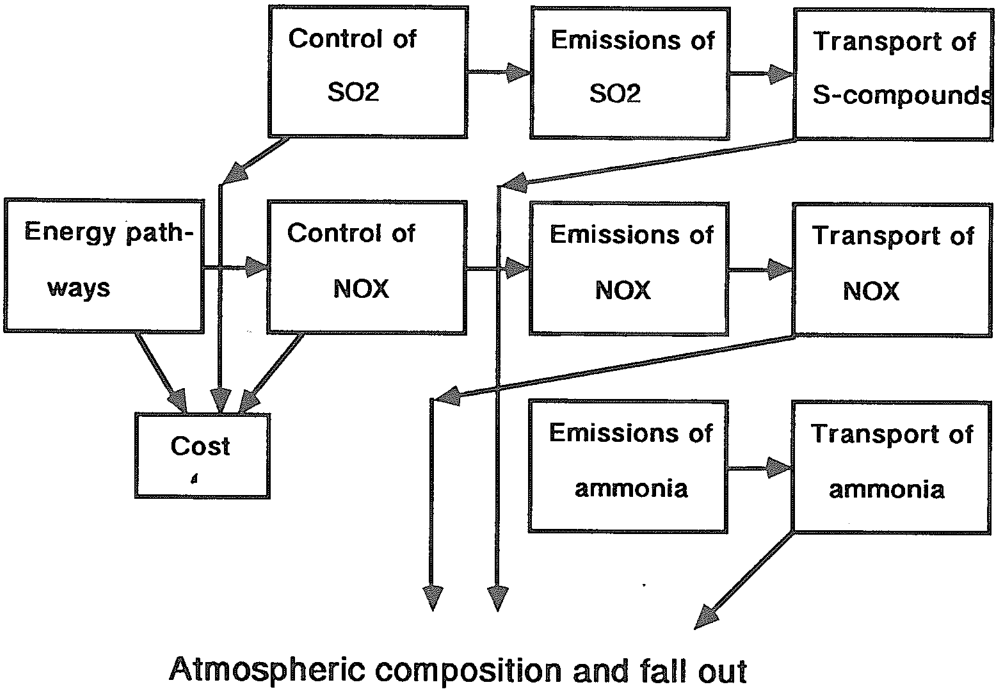

Fig. 5.3 The chains of submodels for emissions, transport and atmospheric processes.

The emissions of sulfur compounds and NOX are based upon the consumption of various forms of energy, their corresponding contents of sulfur and the use of environmental technology, expressed in the following equation:

$$S = E * SE * (1 - p) * (1 - R) \qquad (5.1)$$

where S is the sulfur emission in a box, E is the energy consumption, SE is the average sulfur content relatively to one unit of energy, p is the fraction removed by the environmental technology used according to the environmental legislation and

R is the fraction removed by the combustion process for instance with the fly-ash. A similar equation is used for the emission of NOX.

The transport models are based upon the atmospheric transport due to climatic conditions. Mass conservation equations are set up for each box for the three components, taking into consideration the deposition (the atmospheric fall out), the transport to other boxes and the chemical transformations mainly caused by oxidations for instance of sulfur dioxide to sulfur trioxide, which again forms sulfuric acid by a reaction with water. Six species are considered for the NOX-model: nitric oxide, NO, ozone, uncoupled oxygen, nitrogen dioxide, NO2, nitric acid, HNO3 and nitrate aerosols. Only ammonia and ammonium are considered for the ammonia model, where the ratio of the two species is determined by the pH. The results become the composition of the dry and wet depositions, which need to be translated into environmental impacts.

Figures 5.4 - 5.7 illustrate the use of the submodels summarized in Fig. 5.3. Figure 5.4 gives the present long-term volume-weighted pH in precipitation in Europe (1978 - 1982) and North Eastern America (1980-1984). Figure 5.5 shows the long-term volume-weighted average of sulfate as mg S/ l in precipitation for the same regions and periods. Figure 5.6 compares the time trends of European emissions of sulfur dioxide according to 1) no control scenario and 2) current reduction plans for the 27 countries involved in Europe. The results of the current reduction plans are illustrated in Fig. 5.8, where the isolines for 1 g S / yr*m^2 year 1980 and year 2000 are shown. An improvement is clearly seen, but the isolines should be compared with the fully acceptable level of 0.5 g S / yr*m^2 and the Canadian aim of 0.7 g S / yr*m^2 .

It is therefore understandable that further improvements are discussed on a long-term basis. In the year 2012 a further reduction of the sulfur emission of 30% is foreseen in accordance with a not yet decided but still rather realistic reduction plan, which in addition considers a 20% increase in the energy consumption from year 1990 to year 2012. This plan would almost be able to meet the Canadian aim for the whole of Europe.

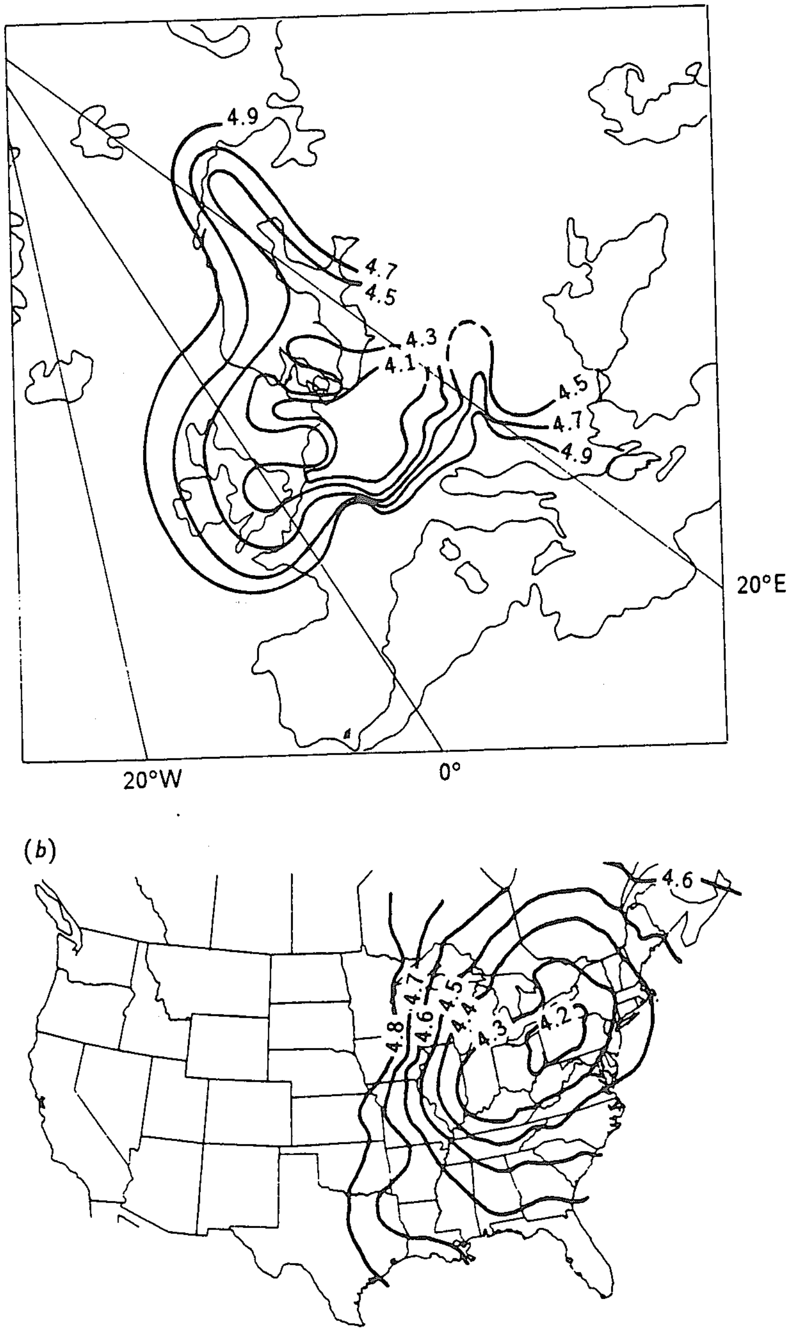

Fig. 5.4 Long-term, volume-weighted averages of pH in precipitation in Europe (1978-1982) and Eastern North America (1980-1984). Sources EMEP /CCC, 1984; NAPAP, 1987. Reproduced from Alcamo et al., 1990 with permission.

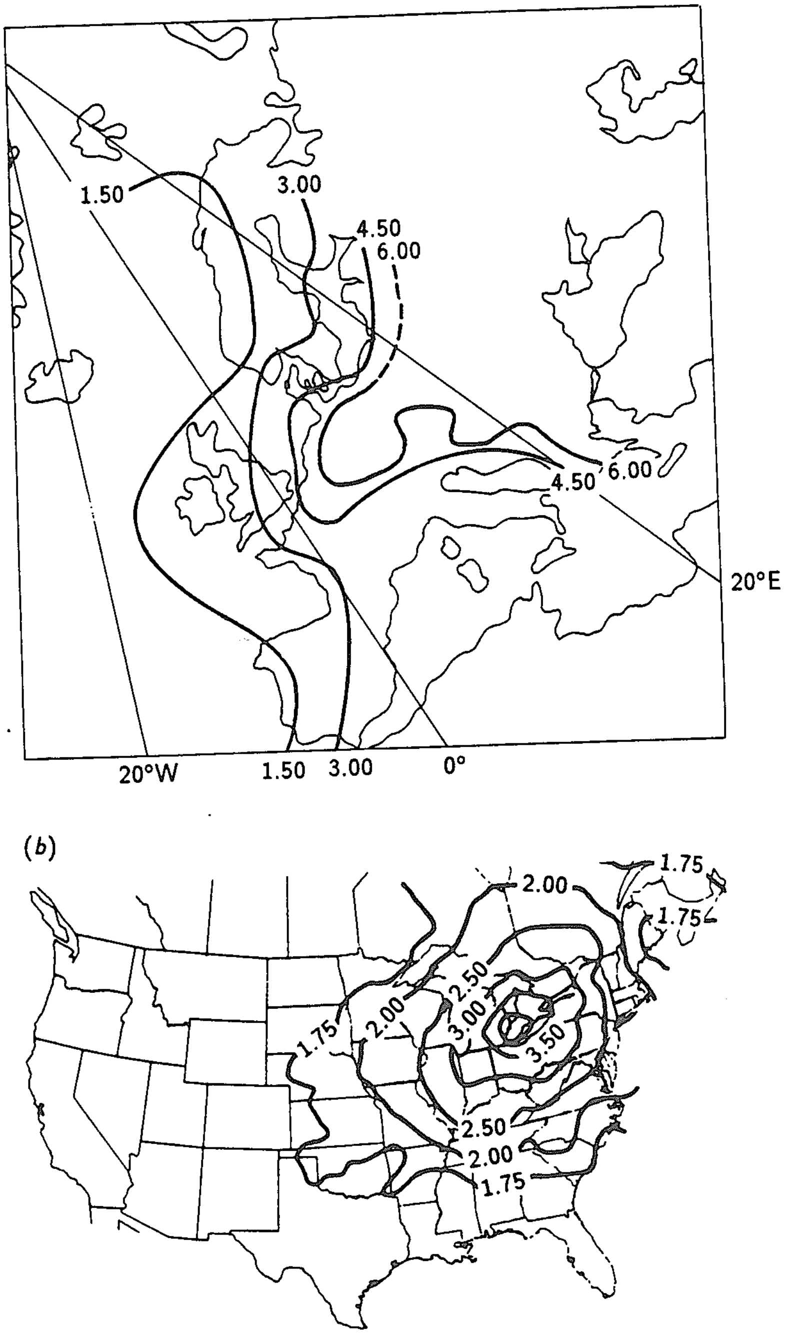

Fig. 5.5 Long-term, volume-weighted averages of sulfur (mg / l) in precipitation in Europe (1978-1982) and Eastern North America (1980-1984). Sources EMEP /CCC, 1984; NAPAP, 1987. Reproduced from Alcamo et al., 1990 with permission.

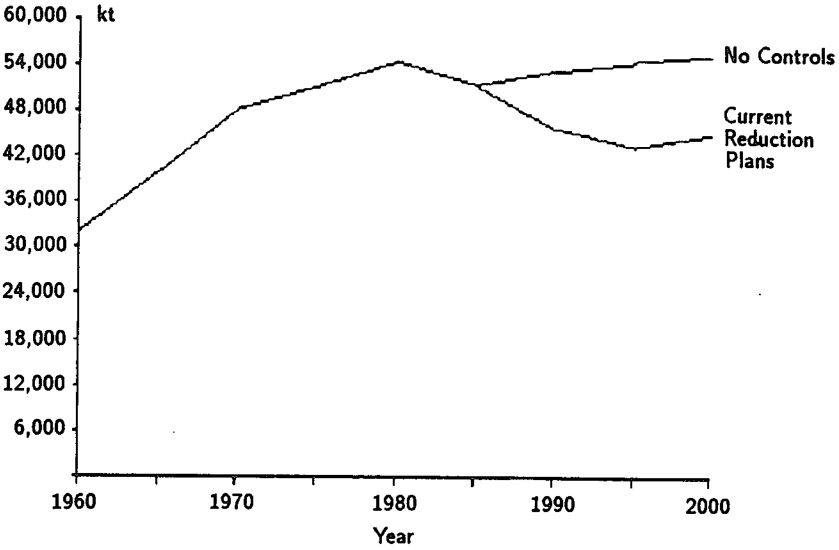

Fig. 5.6 Comparison of time trends of European emissions of sulfur dioxide according to two scenarios 1) no control and 2) current reduction plans for 27 countries. Reproduced with permission from Alcamo et al., 1990 with permission.

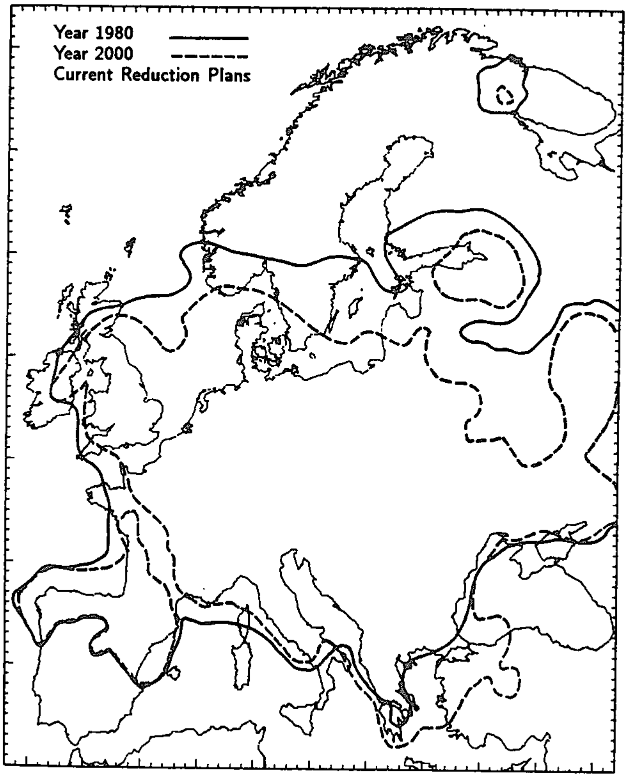

Fig. 5.7 Isolines of 1 gS / yr*m^2 for year 1980 and year 2000 under current reduction plans. Reproduced with permission from Alcamo et al., 1990 with permission.

5.4 Models for Soil Acidity

From the results of the deposition it is possible to estimate the acid load in equivalents of hydrogen ions per square meter per year. In the European model RAINS, acid load is computed from the deposition after accounting for forest filtering and atmospheric deposition of cations (for details; see Alcamo et al., 1990). To organize soil data from soil maps either the grid shown in Fig. 5.2 or the grid used by RAINS using 1°longitude x 0.5 ° latitude may be applied. The Soil Map of the World classifies European soils into 80 soil types. The fraction of each soil type within each grid element is computerized to an accuracy of 5%. The resolution of the RAINS model is such that each grid element includes one to seven soil types, with a mean of 2.2. The following parameters are given for each soil type:

1) Buffering capacity of the carbonate range, BCCA. Unit: keq / ha
2) Buffer capacity of the cation exchange, BCCE, which is the product of total cation exchange capacity, CEC, and base saturation, ß. It is the amount of exchangeable cation reserves. Unit: keq /ha.
3) Buffer rate or the actual dissolution rate of base cations such as magnesium and calcium ions and acid cations such as aluminum ions. In general, the buffer rate corresponds to either the rate of dissolution of calcium carbonate or the dissolution rate of aluminum hydroxide. Unit keq / ha*yr.
4) Silicate weathering rate according to the guideline of Ulrich (1981 and 1983). He reports weathering rates in European soil between 0.2 and 2.0 keq / ha*yr.

The basic computations of the model follow six steps:

1. The weathering rate of silicate minerals is subtracted from the annual acid load.
2. The result of step one is then subtracted from the soil buffering capacity to account for the depletion of the acid neutralizing capacity of the soil. Base saturation and pH are computed based upon these comparisons.
3. In calcareous soil, containing free carbonate, base saturation is not depleted and the soil pH is assumed to stay above 6.2. In non-calcareous soil, as long as silicate weathering keeps pace with the acid load, no decline of pH and base saturation is assumed to occur.
4. If the acid load exceeds the buffer rate of the silicates, the soil shifts into the

cation exchange buffer range and base saturation begins to decline accordingly. The capacity of the cation exchange rate is depleted at a rate equal to the difference between the acid load rate and the silicate buffer rate. pH is computed to decrease according to the decline of base saturation.

5. When base cations are almost depleted, an equilibrium is computed between solid phase aluminum and soil H^+.

6. A recovery of soils is computed in terms of base saturation and pH, when silicate buffer rate exceeds the rate of acid deposition.

The aim of the model is to keep track of the development of soil pH and buffer capacity. Figures 5.8-5.9 illustrate some typical results, that can be obtained by use of the model. Two situations are compared here, soil pH year 2000, if there would be no control and if the current reduction plans are applied.

To simulate flows within the catchment area, the soil is vertically segmented into two soil layers: the uppermost 0.5 m and the deeper parts of soils. The run-off is divided into two flows referred to as quick flow and base flow. The quick flow is mainly in contact with the upper mineral and humus layers, while the base flow is assumed to come from the saturated soil zone. To compute ion concentrations of the catchment flows, the same approach as used in the soil acidification model; see above the six steps of computations. Complete mixing is assumed and chemical equilibrium is assumed to be reached according to computed saturation. The acid load in the soil participates in two processes, cation exchange and release of inorganic aluminum species, the net effect being to provide a buffer for hydrogen ions in the soil solution.

Figure 5.10 gives the summary of processes used in the RAINS catchment model, including its links to the model of lake water chemistry.

Other possibilities to account for the composition of the drainage water will be touched upon in the next section, dealing with the lake water chemistry. It should, however, be mentioned here that Arp (1983) has developed an even more complex model, which is working with n soil layers (n is in practice between 10 and 50) and which takes into considerations the carbon, nitrogen and sulfur cycles. Figure 5.11 gives an overview of the chemical processes considers in Arp's model.

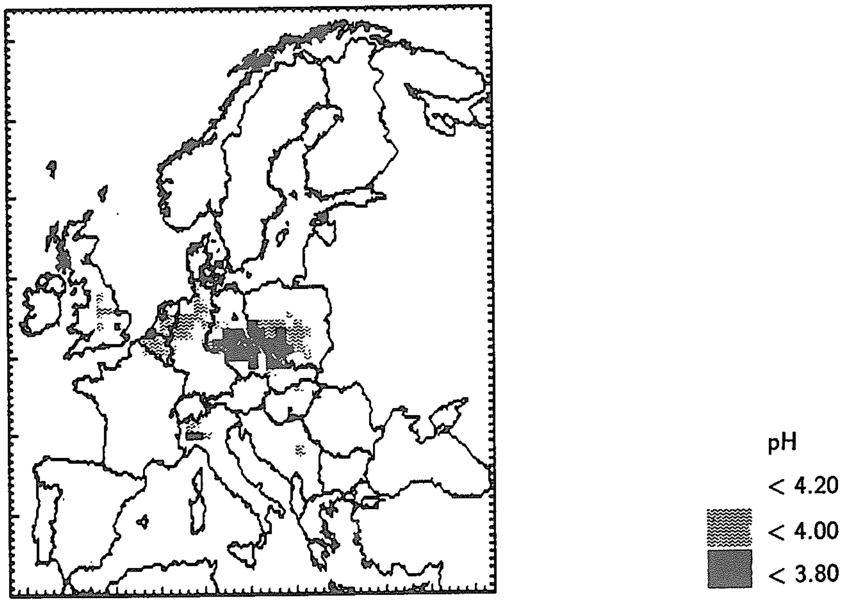

Fig. 5.8 Map of Europe showing pH level of forest soils for no control scenario, year 2000. Reproduced from Alcamo et al. (1990) with permission.

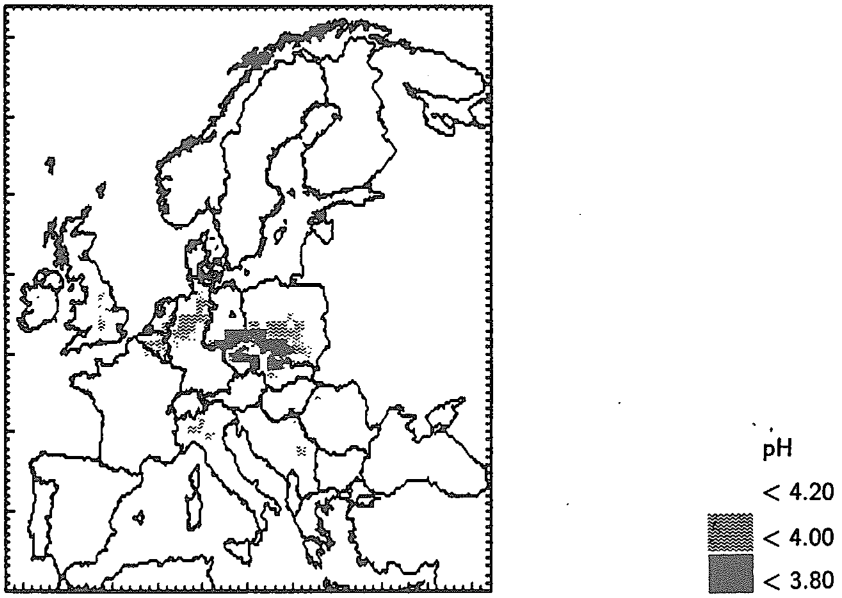

Fig. 5.9 Map of Europe showing pH level of forest soils for current reduction plans, Year 2000. Reproduced from Alcamo et al., 1990 with permission.

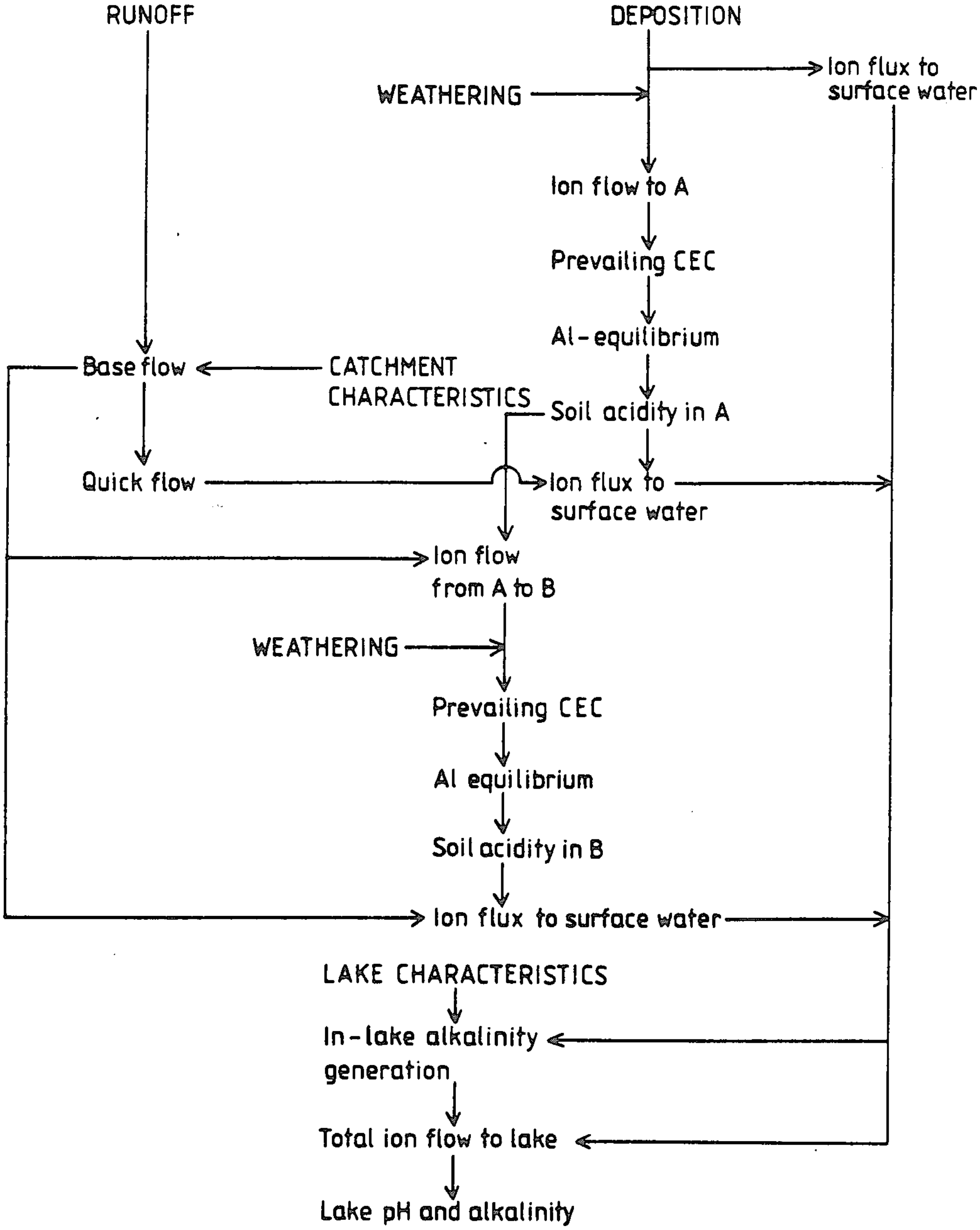

Fig. 5.10 Summary of processes used in the Rains catchment model. Reproduced from Alcamo et al., 1990 with permission.

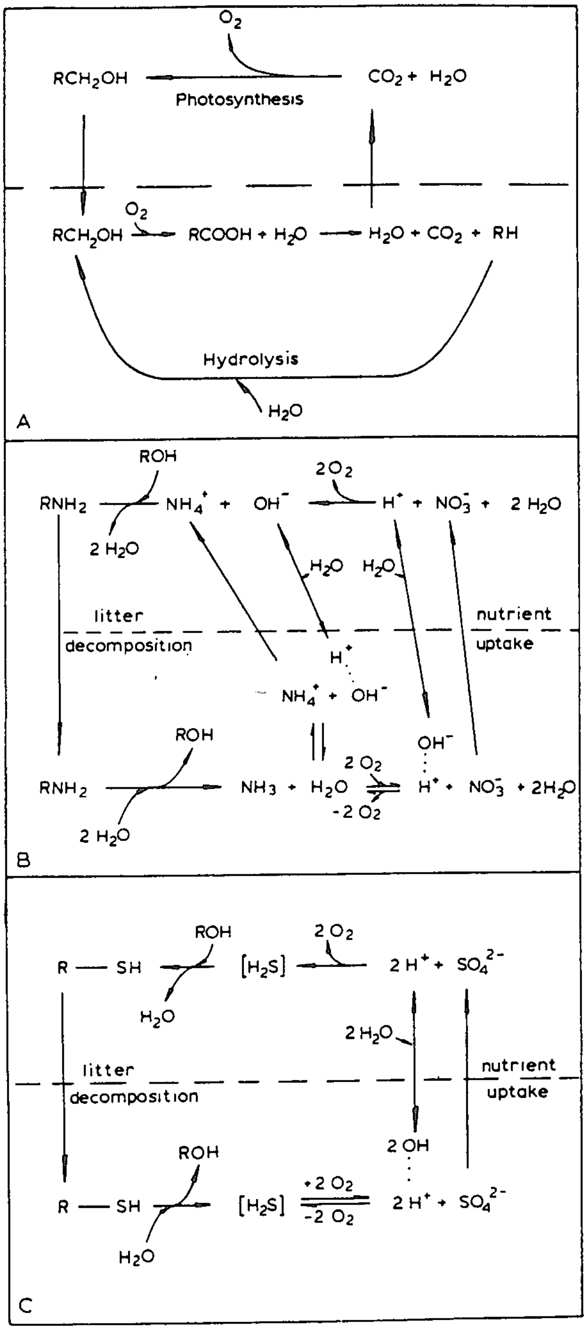

Fig. 5.11. Overview of the chemical processes considers in Arp's model.

It can be concluded that the models of soil processes and of the chemical composition, including the concentrations of various ions and pH, of the drainage water are rather complex. It has not been the intention here to present the models in detail - they are far too complex to be able to do so - but rather to present the difficulties and the basic ideas behind the models. Further details can be found in the references given in this section.

5.5 Modeling Lake Acidification and Lake Water Chemistry

Many approaches have been made on an *empirical* model for the relationship between lake water pH and sulfur load; see Fig. 5.12. Related values of pH and sulfur loads are plotted for a considered catchment area with a given sensitivity for acidification. The curves look like a titration curve. In Fig. 5.12, two plots representing a sensitive and a medium-sensitive area are shown. It can be seen from the plots, that for a sensitive area a sulfur load of less than 0.7 or maybe 0.5 g S/ m^2 *yr. is needed to assure lake pH at 5.3 or above.

Henriksen (1980) has developed a model based upon the assumption that a titration of hydrogen carbonate buffered lakes takes place. Hydrogen carbonate ions are replaced by sulfate ions, which will mobilize the aluminum ions with a corresponding biological effect. The buffer capacity is estimated on basis of the concentrations of non-marine calcium and magnesium ions, while the acid load is estimated from concentration of the non-marine sulfate. Henriksen distinguishes three classes of lakes: hydrogen carbonate lakes, transition lakes and acid lakes with pH and low buffering capacity and consequently low concentrations of non-marine calcium and magnesium ions; see Fig. 5.13. The diagram, Fig. 5.13, can be used to translate concentration of sulfate in the lake water and the concentrations of non-marine calcium and magnesium ions into pH of rain water and to the type of lake (the three classes mentioned above) or to translate pH of rain water and concentrations of calcium and magnesium ions into sulfate concentration and type of lake.

The simple empirical approaches presented in Figs. 5.12 and 5.13 are used without consideration of the drainage water. Weathering processes can, however, be incorporated in the empirical approaches, although the results have little generality, as they are found on basis of regression analysis of local measurements.

RAINS is using, as presented in Section 5.4, a more complex modelling approach to consider the inputs of ions from the catchment area. A nonlinear relationship between the base saturation, β, and the soil pH is used regarding soil chemistry (Reuss, 1983):

$$- \log [H+] = 4.0 + 1.6^{*} \beta^{3/4} \qquad (5.2)$$

where the base saturation is given by β = buffer capacity (BC) / total cation exchange capacity (CEC). If the cation exchange system does not play any role in buffering the inputs to the soil solution, i.e., BC is zero, it is assumed that the equilibrium with gibbsite controls soil buffering. Aluminum is dissolved or precipitated until gibbsite equilibrium is reached:

$$[Al^{3+}] = K_g^{*} [H^{+}]^{3} \qquad (5.3)$$

where the gibbsite equilibrium constant = $10^{2.5}$. Over the long term, the flux of acids and bases into and out of the soil changes the chemical state of the soil. In non-calcareous soil the weathering rate of base cations, wr, largely determines the long-term response of the catchment. As long as the input of base cations from weathering, wr, and from base deposition, db, is larger than the acid load, there will be no change in pH in the soil. If, however, the acid load exceeds the base cation input, the capacity of the cation exchange buffer system is depleted by the rate:

$$dBC / dt = db + wr - df \qquad (5.4)$$

where df is the acid load equal to the total deposition of acid, dt, corrected for the through-fall deposition on forested land and for the fraction of forested land in the relevant grid.

The lake water pH and alkalinity are found from the convective flows Qa and Qb from the two soil reservoirs; see Section 5.4, and the direct input from the atmosphere to the lake:

$$FH = Qa^{*} [H^{+}] + Qb^{*} [H^{+}] + df^{*} AL \qquad (5.5)$$

where FH is the flux of hydrogen ions to the lake and AL is the area of the lake.

The fluxes of hydrogen carbonates originating from the terrestrial catchment, FHC, will contribute to the alkalinity of the lake:

$$FHC = db + wr - df \qquad (5.6)$$

The contribution from the lakes internal alkalinity generation, FL, must be added to FHC to find the total flux of hydrogen carbonates. FL is found with the following equation:

$$FL = dt * ks / (Qt / AL + ks) \qquad (5.7)$$

where ks is the sulfate retention rate coefficient and Qt is the total flow of water to the lake.

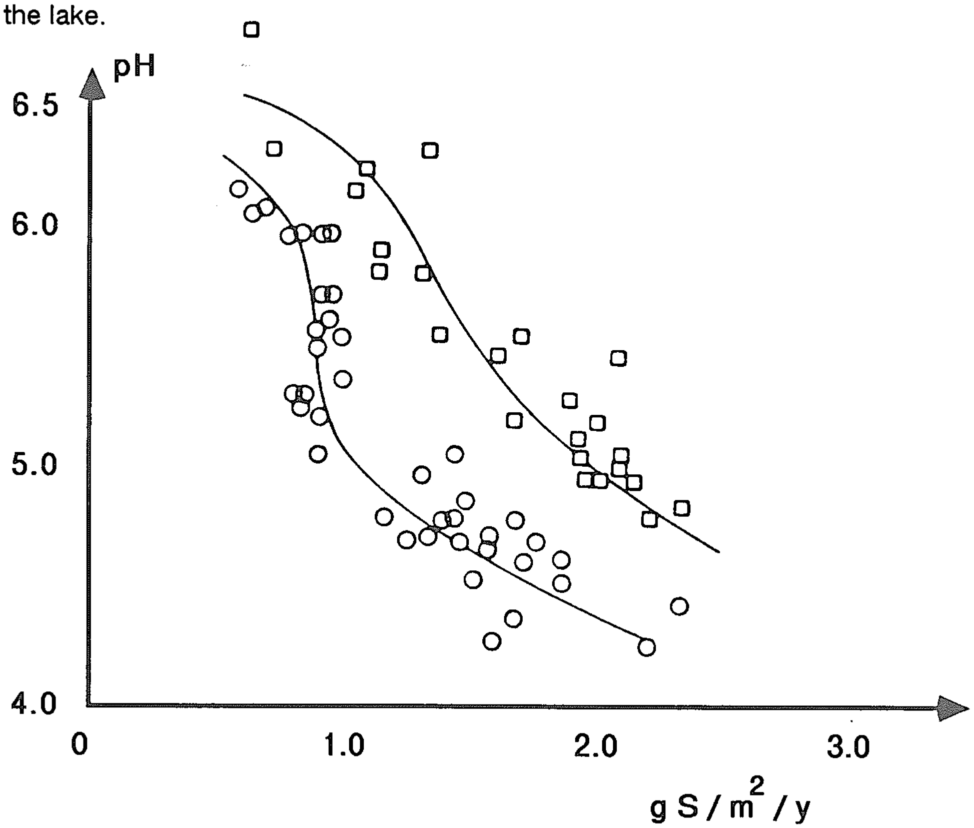

Fig. 5.12 The relationship between pH and sulfur load in g S / m^2 / y. Squares represent a catchment area with medium sensitivity to acidification, while circles are from a catchment area with high sensitivity to acidification.

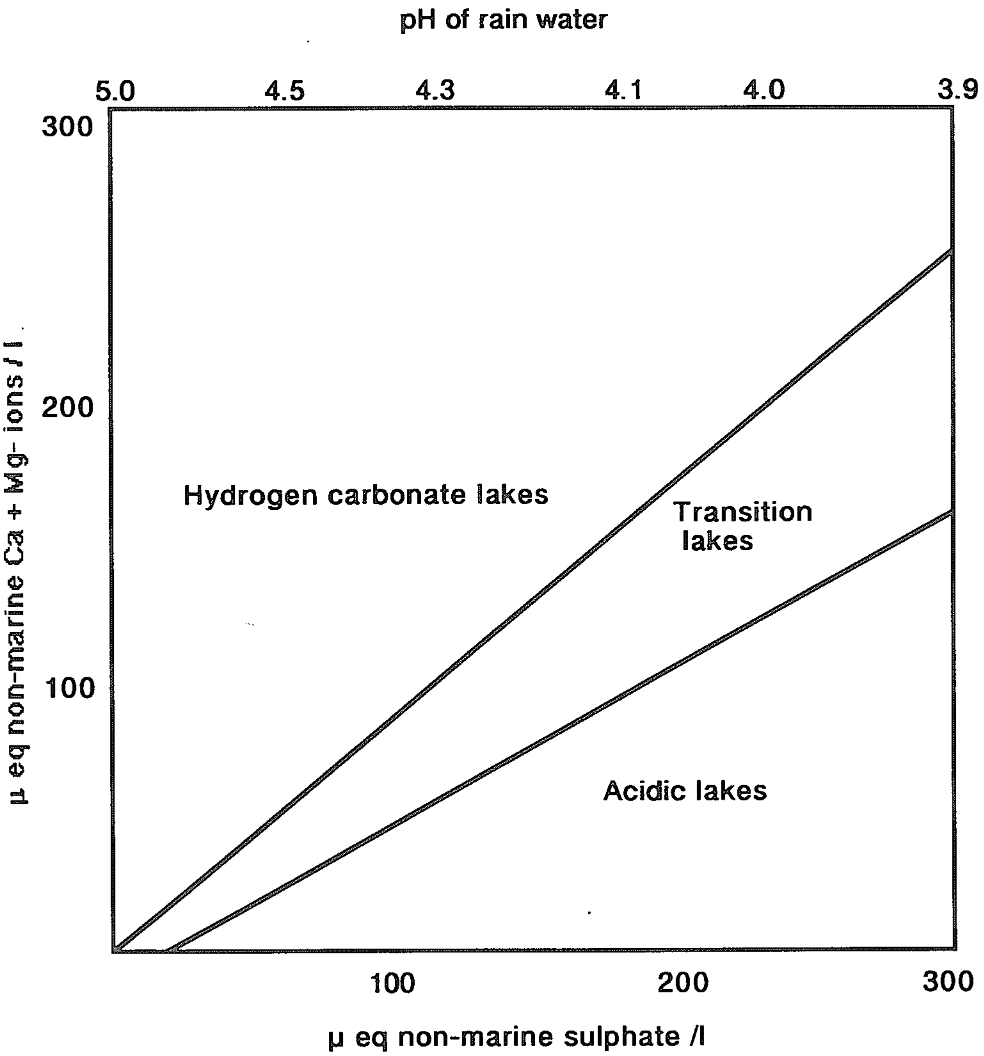

Fig. 5.13. Diagram relating pH of rain water, concentrations of non-marine calcium and magnesium ions and concentrations of non-marine sulfate ions in lake water.

The fluxes of ions mix with the lake water cause a change in the hydrogen carbonate and hydrogen ion concentrations until an equilibrium is reached:

$$[\mathrm{HCO_3^-}] = K1 * H * pCO_2 / [\mathrm{H^+}] \qquad (5.8)$$

where K1 is the first dissociation constant for carbonic acid, H is Henry's law constant for carbon dioxide and pCO_2 is the partial pressure of carbon dioxide in the lake water.

The presented modelling approach has been used on Scandinavian lakes. Figure 5.14 gives the results of the application on the region between Göteborg and Stockholm, named Götaland. It can be seen that the effect of applying control of the emissions on the lake water chemistry is unambiguous.

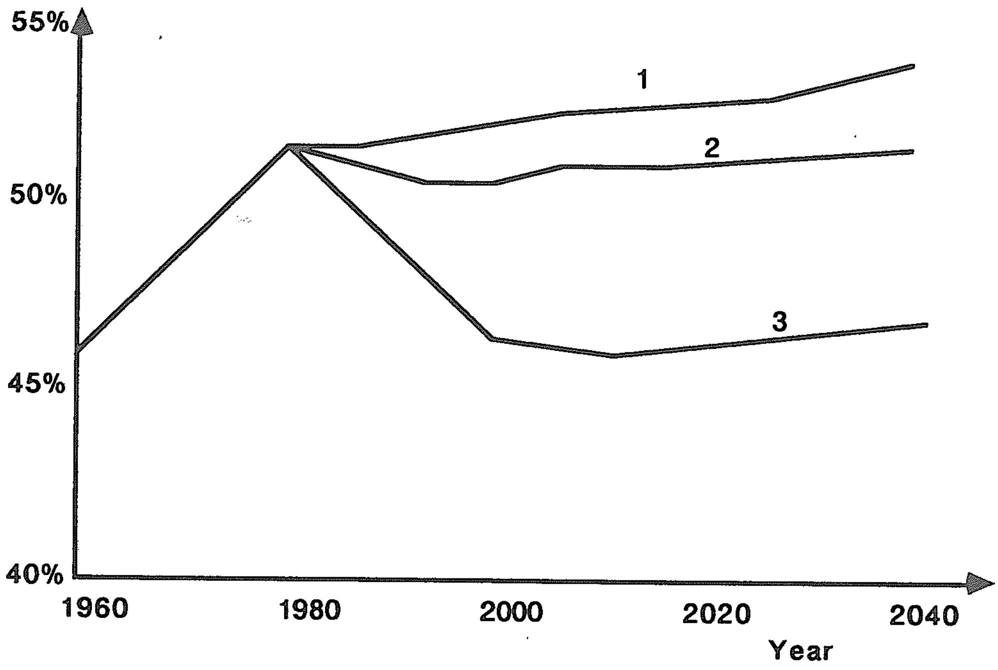

Fig. 5.14 Time trend of percentage of lakes in the Swedish region, Götaland, between Göteborg and Stockholm with pH < 5.3. 1 corresponds to a scenario based on no control, 2 to the scenario of current reduction plans and 3 to the scenario of best available technology. (Alcamo et al., 1990).

5.6 Biological Models of Lake Acidification

Most biological models of lake acidification focus on fish. Brown and Salder (1981) have developed on basis of data for 719 lakes an empirical model, which relates the fish population to pH of the water. They found for the lakes in Southern Norway, that a 50% reduction of the sulfate emission will give an increase in pH of 0.2 in average, which will only improve the fish populations in 9% of the lakes. The model has, however, been criticized for underestimating the relationship between the reduction of sulfate emissions and pH.

Muniz and Seip(1982) have developed another empirical model, in which they distinguish between lakes of different conductivity. Figure 5.15 shows the relationship that they use to translate a change in pH to a probability to find extinguished fish populations in lakes.

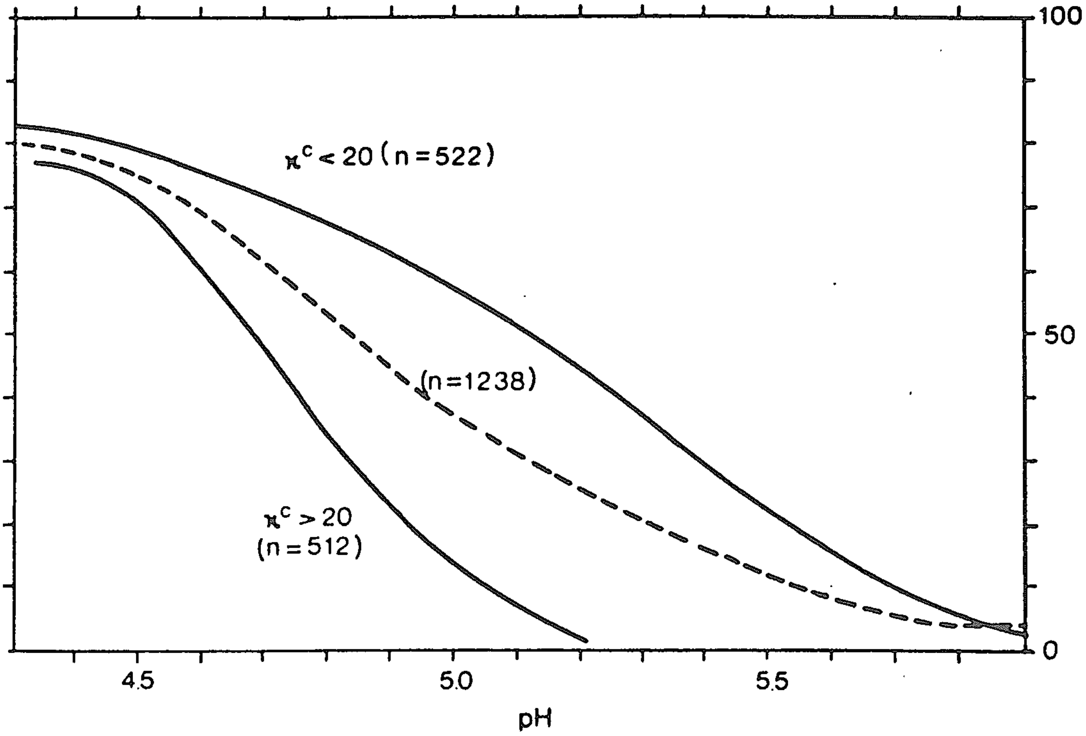

Fig. 5.15 Relationship between percentage of lakes with no fish and pH. The dotted line gives the result of the total number of lakes included in the examination, while the two full lines correspond to a classification of the lakes into two groups: a conductivity above and below μS / cm. n indicates the number of lakes included in the analysis.

Chester, see also Chapter 3 has criticized these two empirical models for not taking into account the role of calcium and aluminum ions. Fish have higher probability to survive low pH at high concentrations of calcium ions (Brown, 1982). Aluminum ions on the other hand will affect the fish populations negatively and a reduced sulfate emission will imply lower concentrations of aluminum ions. Chester has proposed to classify lakes in accordance with the ability of the catchment area to neutralize the acid load. He defines an "effective catchment reactivity", ECR, as:

$$ECR = 1 - [H+] / NMNS \qquad (5.9)$$

where NMNS is the non-marine concentration of nitrate and sulfate. If the hydrogen ions are not retained in the catchment area ECR will be zero, because nitrate and sulfate of non-marine origin is not retained or at the most to a very low extent. Seip et. al. (1984) assert that Chester's classification only reflects the thickness of the soil layer as the lake class with low ECR encompasses lakes at high altitude, where the vegetation is sparse.

Figure 5.15 should under all circumstances be used with precautions, taking into consideration the ion balance of the lake and the catchment area by application of, for instance, Chester's ECR.

5.7 Strategy Development and Assessment Using Models

The details of the models have not been given in this chapter, but only the main ideas behind the chain of models which can be used to assess the relationship between emissions of acid gases and pH of lake water. It is, however, clear from the presentation, that the model chain *is* complex, in spite of the simplifications and the assumption made. The lake acidification model computes only annual means of pH rather than seasonal changes, which is a clear shortcoming of the model results, as the seasonal variability determines the biology of the lakes. The model results agree on the other hand with observed temporal changes in the acidity of lakes. The model chain is therefore a good basis for further development and improvement and offers the best possibility for assessment of the consequences of various scenarios and therefore for the management of regional management strategies.

The planned emission reductions in Europe will unfortunately not lead to a large temporal shift in the distribution of lakes in various pH categories; see for instance Fig. 5.14. It is on the otherhand clear that reduction plans are absolutely needed to escape aggravation of the lake acidification in the coming decades. The current reduction plan shows large improvements compared with the no control scenario.

One point of reference is the critical loads concept, defined as a "quantitative" estimate of exposure to one or more pollutants below which harmful effects do not occur according to present knowledge (Nilsson and Grennfeldt, 1988). Critical loads have been estimated for sulfur and nitrogen deposition for various ecosystems, including lakes, by an international scientific committee under the auspices of the Nordic Council of Ministers and the Economic Commission for Europe. These numbers cannot be strongly defended by scientific findings; however, they do represent a rough consensus of prevailing scientific opinion. The critical load for lakes has been stated to be 0.2 - 1.2 g S / m2 yr. It is based on the most sensitive lakes.

It is a clear limitation of the critical loads concepts, that the actual sensitivity of an ecosystem to depositions of nitrogen and sulfur oxides are very site-dependent. The resilience of a lake to acid deposition depends for instance on the residence time of the lake, the buffering capacity of the catchment area and the level of other pollutants. It is furthermore dependent on the history of pollutants load - all factors, that cannot be captured in a single critical load indication. The modelling approach will offer a better basis for setting management strategies.

It should, last but not least, be stressed that there is no alternative to reduction plans of emissions for the abatement of lake acidification. The application of the ecotechnological methods, presented in Chapter 4, is an excellent supplement to reduction of emissions of nitrogen and sulfur compounds, but unless special conditions prevail, these methods can not stand alone. Implementation of reduction plans is therefore a must and it is highly integrated with the energy and environmental policy of a region in consideration. The problem is consequently very complex to solve. It calls for regional cooperation, for integrated management and for development of sound management models.

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CHAPTER 6

LAGO D'ORTA ECOSYSTEM RECOVERY BY LIMING

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6.1 Introduction

Lago d'Orta is located in north-western Italy, in the watershed of Lago Maggiore (Fig. 6.1). The lake basin, like the other subalpine Italian basins, was created by the glacial erosion of a pre-existing river valley. The drainage basin of Lago d'Orta (97.6 km^2, vs. a lake surface of 18.1 km^2) has subalpine characteristics, with a maximum and median altitude of 1643 and 590 m a.s.l., respectively; the minimum altitude (the lake) is 290 m a.s.l. (Table 6.1). Both the lake and its drainage basin have a long, narrow shape extending in a north-south direction. The areal distribution in the different altimetric bands of the drainage basin is reported in Carollo and Libera (1990).

Lago d'Orta is fed by streams, mainly located in the western part of the watershed, except for the River Pescone which rises in Mottarone (Fig. 6.1). The drainage basins of the tributaries have the following surface areas:

Fiumetta	22.6 km^2
Pescone	18.0 km^2
Pellino	17.5 km^2
Acqualba	8.4 km^2
Lagna	5.0 km^2

These five basins together cover an area equivalent to 73% of the whole emerged lake watershed.

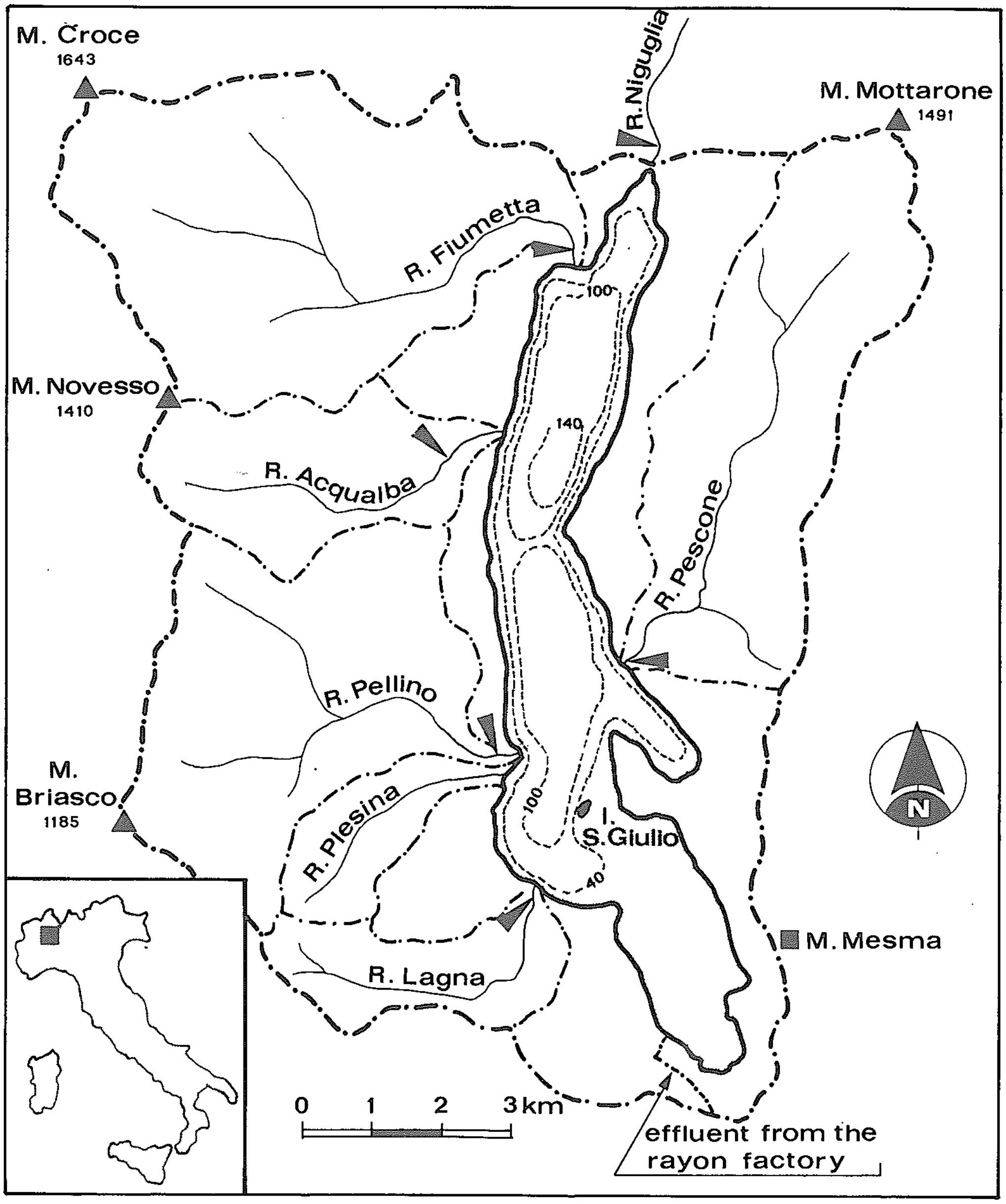

Fig. 6.1 Watershed of Lago d'Orta and sub-basin of the sampled tributaries. Sampling sites for chemical analysis: lake water samples ( ), atmospheric deposition ( ), tributaries and outflow ( ).

Lago d'Orta is the seventh largest Italian lake by volume ($1.3 *10^9$ m^3) and depth (max: 143 m; mean: 71 m). It occupies the south western part of the larger Lago Maggiore drainage basin. Its outlet, River Niguglia (Fig. 6.1), joins the River Strona, a tributary of the River Toce, which flows into Lago Maggiore.

TABLE 6. 1
Main morphometric and hydrological features of Lago d'Orta and its drainage basin.

LAKE		
Mean level altitude	290	m a.s.l.
Maximum length	2.5	km
Mean width	1.4	km
Shoreline length	33.5	km
Area	18.15	km^2
Volume	1.29	km^3
Maximum depth	143	m
Mean depth	70.9	m
Theoretical residence time	8.5	y
DRAINAGE BASIN		
Maximum altitude	1643	m a.s.l.
Median altitude	590	m a.s.l.
Mean width from shoreline	3.68	km
Area (including lake)	115.7	km^2
Water inflow (precipitation)	1900	mm
Mean outflow discharge	4.81	$m^3 s^{-1}$

Lago d'Orta is a warm monomictic lake, usually displaying homeothermy in February with a minimum late winter temperature of 5.6 °C. Some of its characteristics are given in Table 6. 1. It is very important to note that although there is a fairly high mean annual meteoric input (1900 mm y^{-1}) the theoretical water residence time, calculated from the historical mean volume of the outlet (4.81 m^3 s^{-1}), is quite long (8.5 y).

Because of the geology of the catchment basin, mainly formed of gneiss, micashists and granites (Boriani and Sacchi, 1974), the lake water was originally poorly buffered, with total alkalinity ranging from 0.2-0.3 meq 1^{-1} (Monti 1930).

6.2 The Pollution of the Lake

The pollution of Lago d'Orta began at the end of 1926 when a factory (Bemberg) producing artificial silk (rayon) with the cupro-ammoniacal method was established at the southern end of the lake. The process produced waste water (around 0.15 m^3 s^{-1}), heavily polluted with copper and ammonium sulphate, which was collected, summarily treated and discharged into the lake.

Within a few years the chemistry of the lake water was showing clear signs of alteration and the lake was becoming uninhabitable for most of the organisms present. In particular, the zooplankton and the phytoplankton disappeared almost completely, and there was a dramatic decline in the fish fauna, especially of the most valued species (Monti, 1930; Baldi, 1949).

The situation continued to worsen in the following years as regards pH, conductivity and mean annual concentrations of ammonium and nitrate, as well as mean copper and chromium contents (Fig.6. 2).

Starting in the fifties, the data collected by various researchers (Picotti, 1958; Corbella et al., 1958; Tonolli and Vollenweider, 1961a, 1961b) revealed a progressive increase in mean copper concentration in the lake water. Ammonium concentration, on the other hand remained almost constant, below 70 meq l^{-1}, but there was an accumulation in the lake of large amounts of nitrate deriving from the processes of biochemical oxidation of the ammonium which continued to be dumped in the lake by Bemberg.

Moreover, due to the intense activity of nitrification, there was at this time a rapid consumption of the lake's alkalinity which led to increasing water acidification as well as substantial consumption of the dissolved oxygen of the hypolimnion, restored only at the end of the spring circulation (Vollenweider, 1963).

In 1958 a recovery plant was set up by Bemberg and the copper load from the factory was significantly reduced, from a maximum of 80 t y^{-1} to around 1 t y^{-1}; at the same time, however, the factory was continuing to dump loads of untreated ammonium sulphate in the lake, and in addition there was a sharp in-

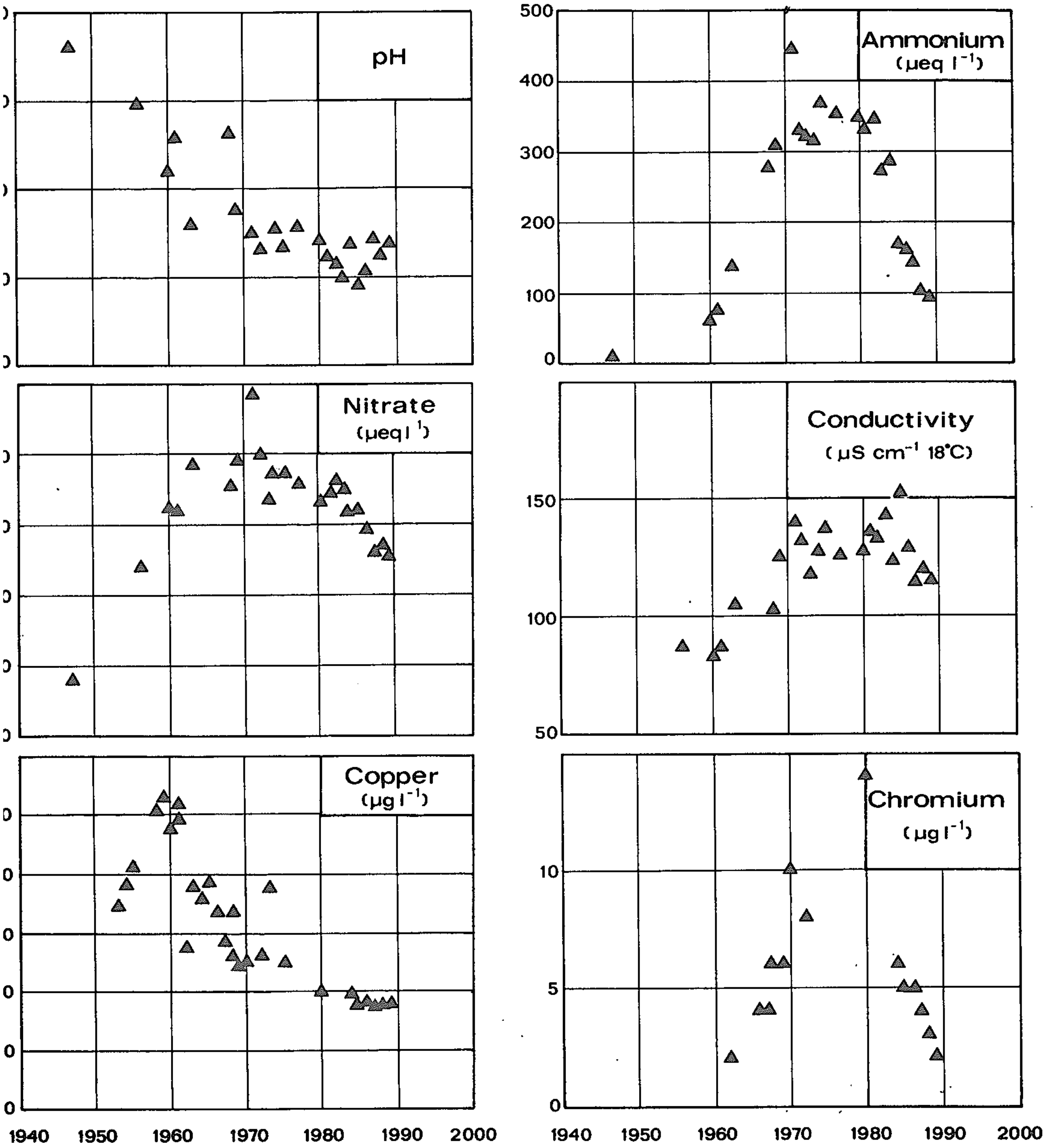

Fig. 6.2 Trend of the main chemical variables in Lago d'Orta (mean concentrations at overturn).

crease in loads of Cu, Zn, Ni and Cr deriving from the electroplating factories on the western shore which at that time were expanding both in number and manufacturing output (Bonacina, 1970; Barbanti et al., 1972; Calamari and Marchetti, 1975).

All the research of the next twenty years, up to the early eighties (summary of references in Bonacina and Bonomi, 1984) continued to record the progressive deterioration of the quality of the lake water (Fig. 6.2), with important alterations which may be summarized as follows:

- marked increase in the mean ammonium concentration (up to more than 400 meq l^{-1}), as a direct consequence of the loads in the Bemberg discharge which were so high as to impair the nitrifying capacity of the lake water;

- accumulation of nitrate up to more than 400 meq 1^{-1}, as an effect of the nitrification processes which were very active up to the 70s, but less intense or frequent in the following decade because of the acidity of the lake water;

- persistent strong acidification of the lake water, as a consequence of the nitrification, with pH between 3.9 and 4.5 units, due to the rapid consumption of the already poor alkaline reserve in the lake and the limited loads of bicarbonate from the watershed;

- mean copper concentration, present in the highly toxic ionic form Cu^{++}, were still high (about 60 mg l^{-1}), in spite of the treatment process initiated by Bemberg in 1958; to the loads from the factory, still present though in lower concentration than in the past, was added the discharge from the plating factories; furthermore these effluents increased the total chromium concentration up to 10 - 15 mg l^{-1}.

6.3 The Years of Recovery

It was not until the beginning of the eighties that there was a real breakthrough in the recovery of the lake. At this time Bemberg set up a treatment plant which improved the yield of copper removal and which, more importantly, permitted an effective removal of ammonium: in 1982 the discharge conformed to the limits of Italian law (10 mg total N l^{-1}) and the total load of ammonium was reduced by more than 95%, from peaks of up to 3000 t N y^{-1} to 30 t y^{-1} while the copper loads decreased from 4,000 to round 300 kg y^{-1}.

TABLE 6. 2
Volume weighted mean concentrations of the main chemical variables at overturn from 1984 to 1988.

VARIABLES			1984	1985	1986	1987	1988
pH			4.36	3.89	4.06	4.42	4.25
Cond. 18 ^{o}C	mS	cm^{-1}	124	149	129	115	120
TA	meq	l^{-1}	0.000	0.000	0.000	0.000	0.000
$N\text{-}NH_4$	mg N	l^{-1}	3.98	2.33	2.20	2.02	1.37
$N\text{-}NO_3$	mg N	l^{-1}	4.46	4.49	4.12	3.82	3.79
TN	mg N	l^{-1}	8.03	7.66	7.15	6.45	5.07
RP	mg p	l^{-1}	2	3	1	2	1
TP	mg p	l^{-1}	7	6	6	1	6
R Si	mg Si	l^{-1}	3.7	4.1	4.2	4.1	4.2
Ca	mg Ca	l^{-1}	6.3	6.5	7.3	7.7	9.1
Mg	mg Mg	l^{-1}	1.5	1.5	1.5	1.5	1.5
Na	mg Na	l^{-1}	5.5	5.4	5.3	5.1	5.0
K	mg K	l^{-1}	1.0	1.1	1.0	1.0	1.0
SO_4	mg SO_4	l^{-1}	30.8	31.4	30.9	31.0	30.6
Cl	mg Cl	l^{-1}	2.5	2.3	2.3	2.3	2.4
Cu	mg Cu	l^{-1}	39	36	37	35	35
Al	mg Al	l^{-1}	90	83	104	95	86
Zn	mg Zn	l^{-1}	62	65	53	51	43
Fe	mg Fe	l^{-1}	58	99	183	83	74
Mn	mg Mn	l^{-1}	98	100	101	119	103
Cr	mg Cr	l^{-1}	6	5	5	4	3
Ni	mg Ni	l^{-1}	-	-	-	18	18

In addition, in 1982 the Lago d'Orta Water Treatment Consortium started up a plant to treat the water discharged from urban and industrial sources on the southwestern shore of the lake. Although there were serious problems in starting the biological treatment, due to the discharge into the sewers of toxic metals in concentrations which were much higher than the permitted levels, the overall removal of the pollution load, was extremely significant (Lacqua et al., 1983).

The response of the chemistry of the lake water in the following years was swift: from February 1981 to February 1985, the mean ammonium concentration dropped from 330 to 160 meq l^{-1}, while the mean copper concentration decreased slightly, from 40 to 35 mg 1^{-1} (Fig. 6.2). The research carried out in those years did not however reveal further signs of a positive alteration in the lake chemistry: pH remained constantly acid in the whole water mass (Fig. 6.2), and the nitrification processes were so slow that it could be predicted that the complete elimination of ammonium, the primary cause of the acidification, would still take many years (Bonacina et al., 1986; Mosello et al., 1986a; 1986b; Bonacina et al., 1988a and 1988b).

The mean volume weighted concentrations of the major ions, as well as those of the trace metals, found at the overturn from 1984 to 1988, are presented in Table 6.2. The values of pH have remained constantly acid. The causes of this situation are not to be sought in loads from the atmosphere, as happens in extensive areas of the earth's surface affected by the phenomenon of acidification of surface waters (Haines, 1981; Galloway and Dillon, 1983; Schuurkes, 1986), but in the nitrification processes occurring in the lake. While most redox processes, whether biological or inorganic in origin, involve the production or consumption of acidity (Stumm and Morgan, 1981), in the case of Lago d'Orta by far the most important process in quantitative terms is the biochemical oxidation of ammonium (Tonolli and Vollenweider, 1961a, 1961b; Vollenweider, 1963; Gerletti and Provini, 1978; Mosello et al., 1986b; Bonacina et al., 1987; Schuurkes and Mosello, 1988; Mosello et al., 1991); its overall reaction is as follows:

$$NH_4^{++} + O_2 <--> NO_3 + H_20 + 2H^+$$

The other mechanisms of production and/or consumption of hydrogen ions and of ammonium, linked to reactions involving autochthon or allochthon organic substances as well as compounds of sulphur, iron and manganese, would appear to be negligible compared to the quantitative variations induced by the nitrification.

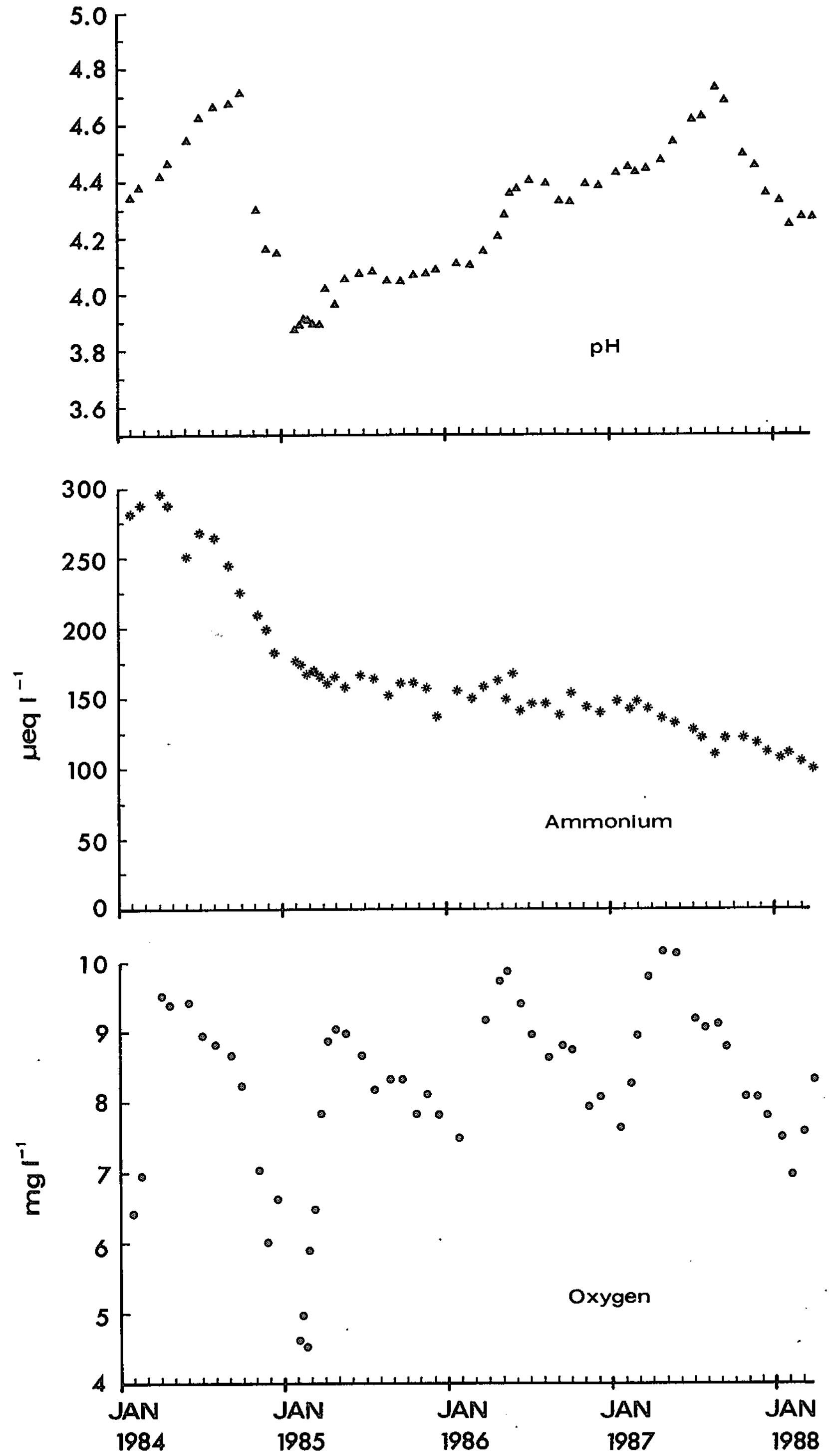

Fig. 6.3. Mean values of pH and mean concentrations of ammonium and oxygen.

In a well-buffered environment the acidity produced by the above reaction would be rapidly neutralized. This cannot happen in Lago d'Orta, as the poor original alkalinity reserve was quickly used up as early as the sixties and, besides, the bicarbonate loads from the watershed are far too inadequate to restore neutral conditions.

Ammonium may therefore be eliminated from the system by two mechanisms: the first is linked to the mass budget, which after treatment of the Bemberg discharge shows a negative balance between input and output; the second is the biochemical oxidation of ammonium to nitrate.

The relative importance of these two mechanisms has varied over the years. Research on nitrification (Vangenechten and Vanderborght, 1980; Roelofs, 1983; Shoen et al., 1984; Schuurkes, 1986) has in fact demonstrated that it occurs at different intensities depending on the pH value. It may begin at pH higher than 4.6-4.8 and stops at pH values below 3.9 units.

During the period 1984-1988, ammonium, while dropping from 4.0 to 1.4 mg N l^{-1} (Table 6.2), did not show a regular decline: the most marked decrease occurred in 1984 and to a lesser extent in 1987, owing to an intense nitrification activity which was highlighted by the net decrease in mean pH, which at the 1985 and 1988 circulations reached values of 3.90 and 4.25 respectively.

The decrease in nitrate was much less pronounced (from 4.5 to 3.8 mg N l^{-1}), because the fraction lost through the outflow or taken up by algae was partially offset by the portion produced through nitrification.

The same aspects are shown still more clearly by an analysis of the seasonal evolution of the nitrification (Fig. 6.3), which occurred largely in the hypolimnion and lasted approximately from August to December. The two nitrification periods in 1984 and 1987 showed, compared to the remaining years, a strong production of acidity as well as a much more marked oxygen consumption mainly in 1984 which, due to thermal stratification, could not be offset by the exchange with the atmosphere. During the months following the minimum levels reached, pH increased gradually due to the alkalinity load from the watershed, until, in summer 1987, it reached values compatible with the resumption of nitrification (4.7-4.8 units): it is thus reasonable to expect that the system will remain acidic until the ammonium has been completely eliminated (Calderoni and Mosello, 1990).

As for the other variables, there were no important variations other than for calcium, which showed an increase from 6.3 to 9.1 mg l^{-1} (Table 6.2). This may be put down to modifications in the Bemberg treatment process, which since 1982 has used calcium hydroxide to neutralize the waste water from the factory.

Comparison for the period 1984-1988 reveals that the ionic balance changed considerably in the period, although it remained highly anomalous because of the absence of bicarbonates and the constant presence of hydrogen ions, due to the persistent acidity of the lake water (Table 6.3). The relative weight of the various ions in 1984 was in the descending series:

$$SO_4^{--} > Ca^{++} = NO_3^{-} > NH_4^{+} > Na^{+} >> Mg^{++} > Cl^{-} > H^{+} > K^{+}$$

In the following years the series changed to:

$$SO_4^{--} > Ca^{++} >> NO_3^{-} >> Na^{+} > Mg^{++} > NH_4^{+} > Cl^{-} > H^{+} > K^{+}$$

The mean trace metal content (Table 6.2) shows significant decreases from 1984 to 1988 for copper (from 39 to 35 ug l^{-1} zinc (from 62 to 13 ug l^{-1}) and chromium (from 6 to 3 ug l^{-1}). In addition to these metals, which derive mainly from industrial waste, there were also high levels of aluminium, due to the partial dissolution in the acid lake water of compounds of this element contained in the inorganic particles conveyed to the lake from the tributaries. Mean aluminium values range between 83 and 104 ug l^{-1}, remaining at lower levels than those found in environments acidified by acid deposition (Henriksen and Wright, 1978; Wright et al., 1980), probably because the acidification of Lago d'Orta involves only the lake water mass and not the whole drainage basin. Seasonal variations of Cu and Al were well correlated to pH, especially in the epilimnion, where the chemistry undergoes considerable variations throughout the year, induced by both biological and hydrological factors (Fig. 6. 4). The highest pH values were recorded in 1984, from May to November, when they were always over 5.0, with a maximum of 6.6 units; a second peak of 5.8 was measured in summer 1987. On these occasions, aluminium and copper both displayed an inverse relation with pH, reaching their lowest concentrations in October 1984 (20 and 12 ug l^{-1} respectively). Similarly, in 1987 the mean aluminium content dropped to 40 ug l^{-1}, while the decrease in copper was less marked (30 ug l^{-1}).

TABLE 6.3

Ionic balance at overturn from 1984 to 1988.

	1984		1985		1986		1987		1988	
	meq l^{-1}	%	meq l^{-1}	%	meq l^{-1}	%	meq l^{-1}	%	meq l^{-1}	%
Ca^{++}	315	15.3	323	15.8	366	18.4	384	20.0	453	23.3
Na^{+}	238	11.6	233	11.4	230	11.5	224	11.6	217	11.1
NH_4^{+}	284	13.8	166	8.1	157	7.5	145	7.5	98	5.0
Mg^{++}	123	6.0	123	6.0	123	6.4	124	6.4	123	6.3
H^{+}	44	2.1	130	6.4	87	2.0	38	2.0	56	2.9
K^{+}	27	1.3	28	1.4	26	1.3	26	1.3	26	1.3
cations	1031	50.0	1004	49.1	989	49.6	940	48.8	973	50.0
SO_4^{--}	641	31.1	653	31.9	644	32.3	645	33.5	637	32.7
NO_3^{-}	319	15.5	321	15.7	294	14.8	273	14.2	271	13.9
Cl^{-}	70	3.4	66	3.2	66	3.3	66	3.4	68	3.5
TA	0	0	0	0	0	0	0	0	0	0
anions	1029	49.9	1040	50.9	1004	50.4	934	51.1	975	50.0

6.4 Chemical Budget

Some tributaries of Lago d'Orta carry a high load of pollutants. This is especially true of the River Lagna, which collects not only discharge from electroplating factories but also urban and industrial sewage from the treatment plant of the Lago d'Orta Consortium. The Qualba and Fiumetta rivers are also polluted, the former by discharge from a tinning factory and the latter mainly by

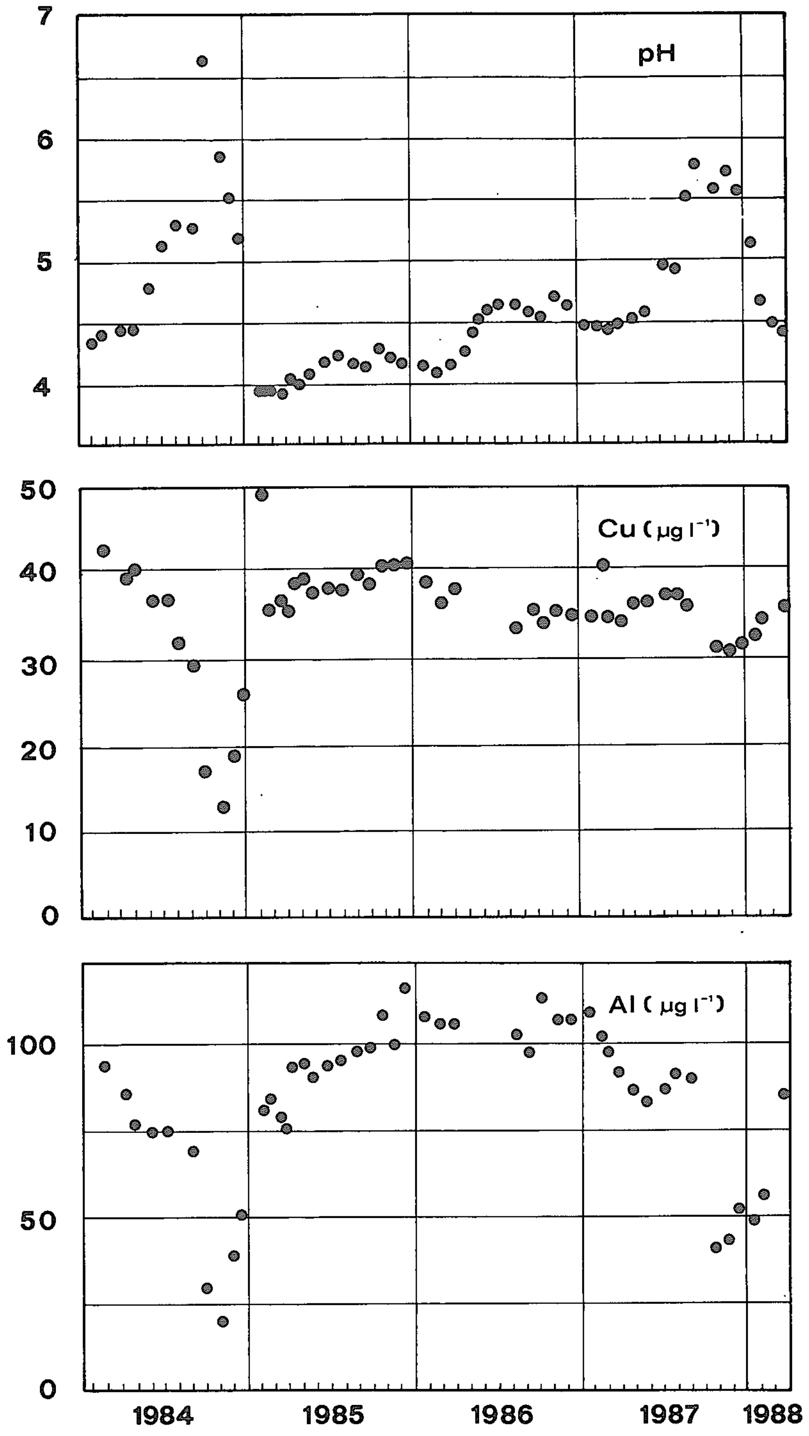

Fig. 6.4 Relationship between pH and mean concentrations of copper and aluminium in the epilimnium.

TABLE 6. 4a

Chemical budget of Lago d'Orta for the period 1984-1989. (units lo^6 eq y-1)

	DRAINAGE BASIN							ATMOSPHERIC DEPOSITION							BEMBERG SEWAGE						
	84	85	86	87	88	89	mean	84	85	86	87	88	89	mean	84	35	86	87	88	89	mean
H^+	0	0	0	0	0	0	0	1.5	0.9	1.2	0.9	1.4	0.8	1.1	0	0	0	0	0	0	0
NH_4^+	2.6	2.0	4.1	3.8	3.0	3.2	3.1	2.2	1.3	2.0	1.9	2.3	1.7	1.9	2.1	2.1	2.0	2.1	2.1	2.1	2.1
Ca^+	41	21	34	49	49	31	37	1.0	1.0	1.0	1.0	1.3	0.6	1.0	45	45	45	45	45	45	45
Mg^{++}	16	8.2	14	20	20	14	15	0.3	0.2	0.3	0.3	0.3	0.2	0.3	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Na^+	31	15	27	32	32	26	27	0.4	0.2	0.4	0.4	0.4	0.3	0.4	5.2	6.1	5.7	6.5	6.0	6.1	5.9
K^+	3.3	1.6	3.1	4.0	4.0	3.2	3.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
cations	94	48	82	109	108	77	86	5.5	3.7	5.0	4.6	5.9	3.8	4.7	53	54	54	55	54	54	54
HCO_3^-	41	21	36	14	43	39	37	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	6.0	5.7	7.0	6.0	6.0	5.8
SO_4^{--}	31	16	28	35	34	20	27	3.1	1.8	3.0	3.0	3.0	2.1	2.7	45	45	45	45	45	45	45
NO_3^-	10	5.6	10	12	11	8.5	10	0.6	0.3	0.5	0.5	0.4	0.3	0.4	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cl^-	14	5.9	11	15	18	11	12	1.8	1.5	1.8	1.5	1.9	1.7	1.7	0.4	0.4	0.4	0.4	0.4	0.4	0.4
anions	96	48	84	106	106	79	87	5.5	3.6	5.3	5.0	5.3	4.2	4.8	50	52	52	53	52	52	52

urban sewage. The Pellino and Pescone rivers present a better picture, although episodes of industrial pollution have occasionally been recorded.

As the area drained by the tributaries covers 73% of the drainage basin, the chemical load has been extrapolated to the remaining 27% of the contributing area. The Bemberg loads have been estimated both on the basis of monthly samples taken at the discharge point during 1984-1985 (Mosello et al., 1986b), and from analyses supplied by the firm which were checked by occasional direct measurements. The main source of the loads considered, apart from hydrogen ions, calcium and sulphate, is the drainage basin; the hydrogen ion load derives exclusively from atmospheric precipitation on lake surface (Tables 6.4a and 6.4b).

TABLE 6.4b
Chemical budget of Lago d'Orta for the period 1984-1989
(units 10^6 eq y^{-1})

	TOTAL INPUT							OUTPUT						
	84	85	86	87	88	89	mean	84	85	86	87	88	89	mean
H^+	1.5	0.9	1.2	0.9	1.4	0.8	1.1	1.4	1.2	1.5	1.7	1.7	1.5	1.5
NH_4^+	6.9	5.4	8.1	7.1	7.4	7.0	7.1	34	15	21	17	17	8.5	19
Ca^{++}	87	67	80	95	95	77	83	63	36	55	77	78	53	60
Mg^{++}	17	9.4	15	21	21	15	17	22	12	18	20	21	14	18
Na^+	7	21	33	39	38	32	33	41	23	33	35	34	23	31
K^+	3.5	1.8	3.3	4.2	4.2	3.4	3.4	5.0	2.5	4.0	3.7	4.0	2.9	3.7
cations	153	106	141	168	168	135	145	166	90	133	154	156	103	134
HCO_3^-	45	27	41	51	49	45	43	2.0	0.0	0.0	2.4	2.1	3.7	1.7
SO_4^{--}	79	63	76	83	82	67	75	100	50	80	106	104	70	85
NO_3^-	12	6.9	11	14	12	10	11	13	6.0	10	10	11	7.1	9.4
Cl^-	16	7.8	13	17	20	13	15	48	31	42	38	40	26	38
anions	152	104	142	165	164	135	144	163	87	132	156	157	108	134

This is also confirmed by comparing the in-lake concentrations measured at the overturns 1988 and 1989 with the mean content found in the period 1984-1987, both in the atmospheric deposition (volume weighted means) and in the inflowing water (values weighted according to the watershed area from the mean annual concentration of the main tributaries) (Table 6.5).

Although the atmospheric deposition is decidedly acid (mean pH for the period 4.42 units); no episodes of acid loads to the lake were recorded, not even during the frequent events of heavy atmospheric precipitation.

The ammonium contribution deriving from atmospheric deposition on the lake is also important; of the same proportions as that contained in the Bemberg discharge (1.3 against 2.1 Meq y^{-1}), it is slightly less than the load coming from the drainage basin (3.1 Meq y^{-1}) (Table 6.4a).

TABLE 6.5
Mean values in the period 1984-1987 of pH, conductivity and mean concentrations of atmospheric deposition (A) and inflowing waters (B), compared with the lake chemistry at overturn 1988 (C) and 1989 (D).

VARIABLES		A	B	C	D
pH		4.42	7.36	4.25	4.45
Cond. 18 °C	mS cm^{-1}	30	67	120	112
H^+	meq l^{-1}	38	0	56	35
NH_4^+	meq l^{-1}	62	27	98	86
Ca^{++}	meq l^{-1}	38	298	453	456
Mg^{++}	meq l^{-1}	9	119	123	126
Na^+	meq l^{-1}	13	213	217	212
K^+	meq l^{-1}	4	25	26	26
HCO_3^-	meq l^{-1}	0	293	0	0
SO_4^{--}	meq l^{-1}	91	218	637	637
NO_3^-	meq l^{-1}	53	96	271	250
Cl^-	meq l^{-1}	16	75	68	67
cations	meq l^{-1}	164	682	973	954
anions	meq l^{-1}	160	682	975	942

The largest loads of calcium and sulphate derive from the Bemberg discharge, as a consequence both of the manufacturing process (use of copper and ammonium sulphates) and of the final neutralization of the waste water with calcium hydroxide.

Moreover, it should be noted that the sulphate load from the tributaries is considerably greater than might be expected from the lithology of the catchment and from the atmospheric precipitation over the whole drainage basin. As the areal contribution from the basin (0.28 eq m^{-2} y^{-1}) is almost twice that of the precipitation (0.15 eq m^{-2} y^{-1}) and there are no mineral formations which can explain this considerable difference, the origin must be traced to industrial loads especially from the watersheds of the rivers Lagna and Qualba.

6.5 The Potential Alkalinity Model

Given this hydrochemical situation, the time required for the lake to return to "natural condition", that is, the reconstruction of an alkaline reserve balanced with the loads from the catchment and the complete removal of ammonium, depends essentially on two mechanisms.

The first of these is linked to the mass budget which, in the case of ammonium, has shown a negative balance between input and output, since Bemberg started treating their waste. In fact, during the period 1984-1988, the loads of ammonium entering the lake have always been much lower than the output (Tables 6.4a and 6.4 b). It should be noted, however, that the removal rate of ammonium, according to this mechanism, tends to become slower in time, because the difference between input and output becomes progressively less as the in-lake concentration is reduced.

The second mechanism operates through the oxidation of the ammonium to nitrate. This process has not been continuous over the years, as its rate is strictly dependent on the acidity produced by the nitrification itself.

In order to take both mechanisms into account, a model was used (Vollenweider, 1975) which considers the mean lake concentrations, weighted on the volumes of the different water layers sampled at the overturn, and assumes that the variation of a conservative substance in the lake is a function only of input and out put, with no other significant sources or losses:

$$\frac{dM_W}{dt} = v_i [m_i] - v_w [m_w] \qquad (6.1)$$

where M_w is the in-lake mass of the substance, m_i and m_w are respectively the mean concentrations of inflowing and outflowing waters, v_i and v_w are inflowing and outflowing volumes of water.

Keeping in mind the importance of ammonium oxidation as a source of acidity for the lake, the model uses the variable potential alkalinity' P*Alk* defined as:

$$[PAlk] = [m_w] = [TA] - [H^+] - 2 * [NH_4^+] \qquad (6.2)$$

where [TA] is the total alkalinity, defined and measured following A.P.H.A. (1989), $[H^+]$ is the hydrogen ion concentration, calculated from pH, $[NH_4^+]$ is the ammonium concentration expressed, as are the other variables in meq l^{-1}

The value of the difference between [TA] and $[H^+]$, if positive, corresponds to actual conditions of alkalinity in the lake mass: if it is equal or close to zero, it indicates a theoretical pH of about 5.6 units in equilibrium with the atmospheric CO_2; if negative, it is evidence of real acid conditions.

The term 2 * $[NH_4^+]$ represents, on the other hand, the potential acidity, that is, the acidity which would be produced stoechiometrically by the complete oxidation of the ammonium to nitrate.
The solution of equation 1 gives:

$$[m_w]_t = [m_w]_{t0}\, e^{-r(t-t0)} + l_m / r \; [1 - e^{-r(t-t0)}] \qquad (6.3)$$

The net alkaline loads from the watershed l_m expressed in meq m^{-3} y^{-1} of lake water, were calculated in the same way, taking into account the mean loads of bicarbonate, hydrogen ion and ammonium measured during 1984-1988 (Tables 6.4a and 6.4b). The values assumed for the constants of the model are as follows:

$[m_w]_{t0}$ = - 750 meq m^{-3}. Value of the potential alkalinity deficit measured at the time t_0 (April 1982), the first year after the start of the treatment of the Bemberg waste.

r = 0.12 y^{-1}. Theoretical flow coefficient, based on the 30 year historic mean of the outflow discharge.

l_m = 21 meq m^{-3} y^{-1}. Mean volumetric load per unit of lake volume of net alkalinity for the period 1984-1988.

Fig. 6.5 compares the time variations of the potential alkalinity deficit forecast by the model (continuous line), with the values measured at the circulation from 1982 to 1988. Moreover, as an indication of the variability of the estimate, the figure also shows the trends obtained by using the following extreme annual values, found during the period under consideration:

maximum (broken line) l_m = 26.5 meq m^{-3} y^{-1}; r = 0.15 y^{-1}
minimum (dotted line) l_m = 11.8 meq m^{-3} y^{-1}; r = 0.10 y^{-1}

As the figure shows, despite the implied simplifications of the model, outflowing concentrations identical to the mean in-lake concentrations, i.e. absence of chemical stratification), the experimental points show good agreement with the trends forecast.

This suggests that such an approach is reliable and can give useful indications of recovery times for the lake, supposing that the bicarbonate and ammonium inputs remain of the same magnitude as in recent years.

A cautious prediction therefore was made that the alkalinity deficit could not be eliminated before 1996, after which date another 15 years would be required to reach an alkalinity level in equilibrium with the loads from the watershed. Without any intervention, Lago d'Orta was clearly bound to remain polluted for many years, with no possibility of real recovery the water would remain extremely acidic until 1996, as it has been for that matter during the last 20 years. This situation implied serious consequences for the whole ecosystem, which may be summarized as follows:

- the rate of nitrification would be enormously reduced, as the process can begin again only when pH is over 4.7-4.8 units; this would contribute to prolonging the time required to eliminate the ammonium in the lake;

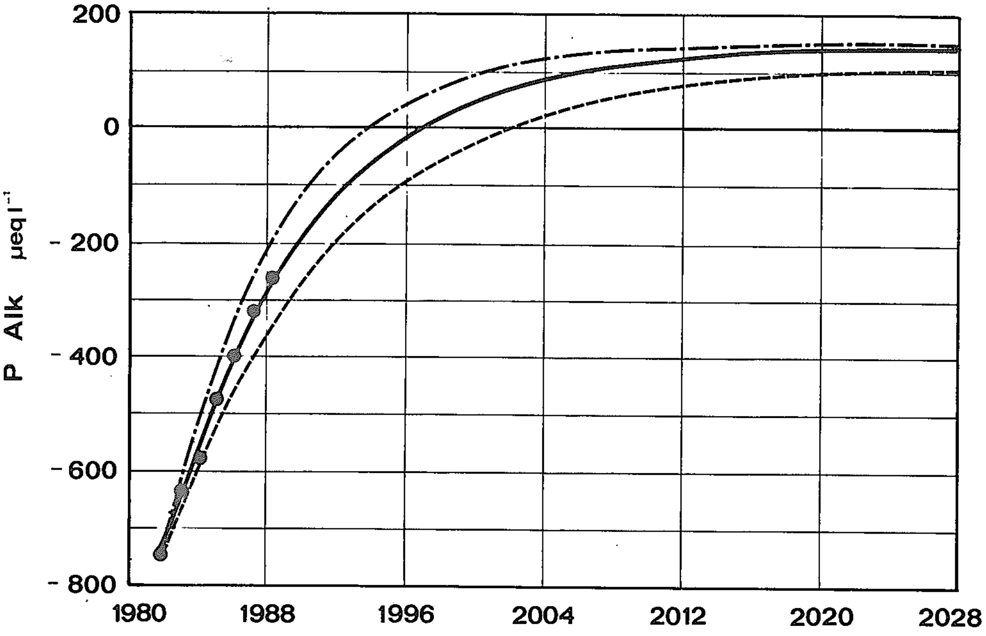

Fig. 6.5. Evolution of P*Alk* following the input-output model (full line), compared with the experimental measurements (dots). For details see the text.

- metals such as Cu, Al, Cr, Ni would remain in solution in their most toxic form;

- the biological community would be destined to remain highly anomalous, unstable and with a low number of species;

- all the uses to which the lake water is put would continue to be seriously compromised, including its use as a recreational resource, of prime importance in a tourist area such as that of Lago d'Orta. Already in 1938 bathing was prohibited in some parts of the lake because the acidity of the water exceeded the legal limit.

6.6 The Liming Project

It was thus a rather gloomy picture which emerged from this situation, despite the signs of recovery, which in any case would be a lengthy process, and the lake would not be a viable entity for many years to come. This would negate the beneficial effects of the treatments which had already been carried out, and would deny the possibility of recovery to one of the most important freshwater reserves in Italy. With these considerations in mind, the CNR-Istituto Italiano di Idrobiologia advanced the proposal of a "Plan for a direct recovery intervention", through a liming operation (Calderoni et al, 1990).

The potential alkalinity model proposed for the lake (Fig. 6.5.) shows that the total alkalinity deficit since January 1988 is 262 meq m^{-3}. This amount is equivalent to 17,000 t of pure $CaC0_3$. With a conservative estimate of 75% dissolution, made on the basis of the empirical models of Warfvinge et al., (1984) which take account of the initial pH, the mean depth and the different kinds of carbonate, it was calculated that a total of about 23,000 t was required for the liming. The operation was to be carried out with the aid of boats and suitable equipment, by spreading a semiliquid suspension of calcium carbonate on the lake surface, starting from the southernmost zone, in successive batches. The products used for the purpose would have to be of natural origin, such as limestone or calcite, finely powdered, free from marl or clay and with a minimal content of toxic metals.

The proposal was put forward in collaboration with the public bodies directly interested in the recovery of the lake: the Province of Novara, the Lago d'Orta Water Treatment Consortium, the Comunita Montana Cusio Mottarone, the two Health Boards responsible for the area and the Lago d'Orta Tourist

Board.

The project was approved and adopted by the Provincial administration and the Piedmont Region, who submitted an application for funding to the Ministry of the Environment. The application was in its turn approved by the ministry and the bureaucratic procedure for obtaining the funds initiated.

The technical side of the project was defined in the light of experience gained in some northern European countries (summary of references in Bengtsson et al., 1980: Bjerle et al.. 1982; Sverdrup and Bjerle, 1982, 1983; Warfvinge et. al., 1981; Lessmark and Thornelof. 1986), where the technique has for many years been employed to neutralize lakes acidified by atmospheric deposition.

The results of laboratory tests on lake water samples (Mosello et al., 1989) were also taken into account; these samples, which had an initial pH of 4.0 units, were treated with different amounts of $CaCO_3$ and analysed weekly over a two-month period. The addition of calcium carbonate increased the pH to a maximum of 7.2-7.5 after 2 weeks. The lowest concentrations of metals were measured in these samples. This is in accordance with the field observations, which shoved the strict relationship between pH and metal concentration (Fig. 4, Mosello et al., 1986a).

The results obtained from both lake and laboratory experiments were generally in good agreement with those expected from the known chemical equilibria controlling the concentrations of the metals studied. They suggested that a notable decrease in trace metal concentration in Lago d'Orta was to be expected as a result of an increase in pH to values above 6.0. The increase should, however, take place throughout the whole water mass of the lake, to avoid the redissolution effects occurring when oxy-hydroxides come into contact with water layers which are still acid, as was observed in autumn 1984.

6.7 Liming operation

The calcium carbonate used for the liming was a finely powdered natural limestone, containing about 20% water. Its particle size distribution is shown in Fig. 6.6. The dry limestone is composed of 92% $CaCO_3$, 6% $MgCO_3$

and 2% impurity, mainly clay-free silica, with a very low trace metal content (Table 6.6).

Fig. 6.6. Particle distribution curve of the powered lime used in Lago d'Orta.

The spreading was done from a boat equipped with a tank (about 80 tons), a concrete mixer (9 m^3), a mixing tank (10 m^3), and a jet pump for spreading the slurry, made with lake water. About 80 tons of limestone was added to the lake daily (400 tons per week) with interruptions in August, September and January-February (Fig. 6.7). The first liming was done in the southern part of the lake, i.e. the part farthest from the outflow. Operations were halted in winter due to the slurry freezing in the pipes and tanks, but resumed in the period March-June 1990 when the slurry was spread once again on to the lake surface.

TABLE 6.6
Metal content of the limestone used for the liming (mg kg^{-1} dry powder)

Al	950	Mn	30
Cr	7.2	Ni	2.7
Cd	0.07	Pb	2.2
Cu	1.2	Tl	<0.5
Fe	278	Zn	5.4
Hg	0.01	Ti	2.6

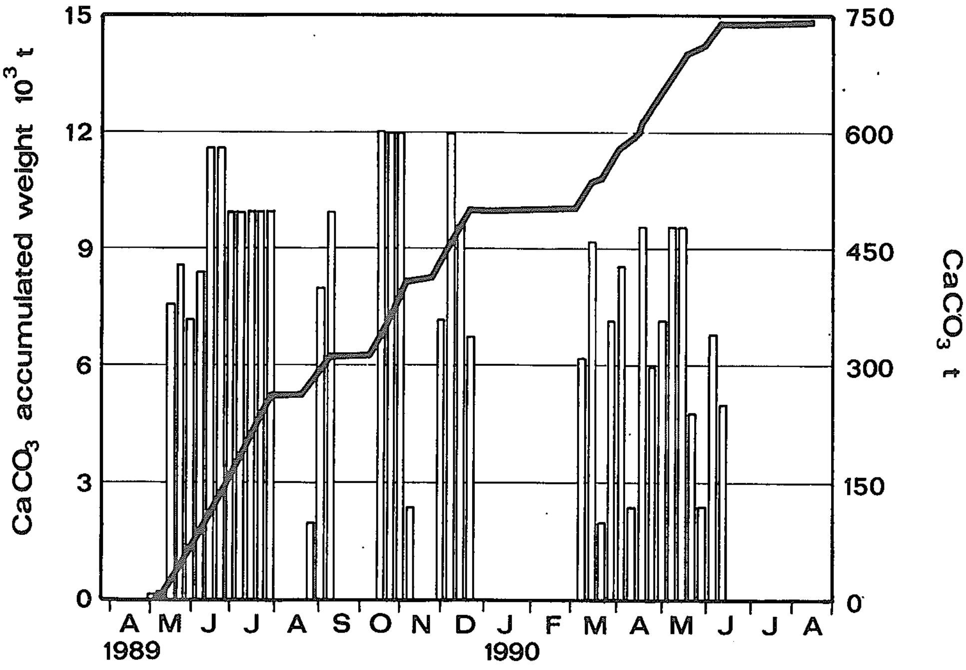

Fig. 6.7. Accumulated (full line) and weekly (bars) amounts of natural limestone added to Lago d'Orta.

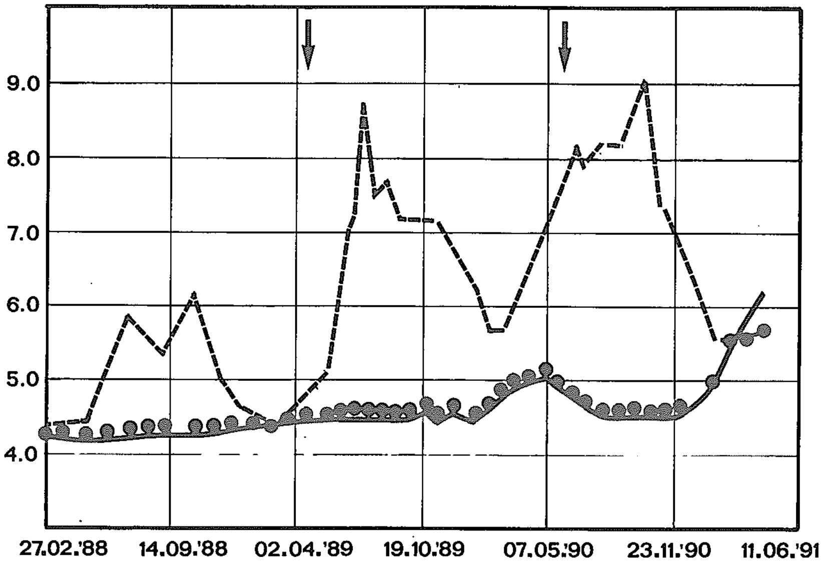

Fig. 6.8 Epilimnetic (broken line), hypolimnetic (full line) and mean pH (dots) in Lago d'Orta. The arrows indicate the liming periods.

A total of 1,800 t of pure calcium carbonate was added to the lake between May 1989 and November 1989 and the remaining amount of 6,100 t was spread between March and June 1990.

During the trials and for the first three weeks of liming, the procedure was continuously monitored to establish and refine the various technical parameters to be used in preparing the suspension and adding it to the lake, compatibly with the spreading technique adopted and the daily quantities to be added. For this purpose a multiparametric sounding device was used which was able to measure and record depth, temperature, light transmittance, conductivity and pH. Other surveys were carried out at the same time by researchers of the CNR, Istituto di Ricerche sulle Acque of Brugherio and by the Ispra Joint Research Centre of the European Community.

In this way, by means of immediate measurements and an examination of the vertical profiles of pH and transmittance in the hours and days following the spreading, it was found that the best results, in terms of performance or the liming equipment and solubilization yield of the carbonate, were obtained if suspensions containing from 25 to 35% dry material were used.

In July 1989, when a marked thermal stratification became established, it was realised that the carbonate suspension was having great difficulty in reaching the still acid profundal zone of the lake and was being induced by the surface currents to affect the whole epilimnic water mass, and was tending to leave the lake through the outflow, more than 5 km north of the spreading zone. Analyses of pH, total alkalinity and calcium showed that the carbonate was being diffused over the whole lake, particularly in the layer from surface to 30 m. Consequently, from the middle of July, the suspension was added by gravity below the thermocline, using a vertical pipe (diameter 0.35 m, length 14 m) anchored to the boat.

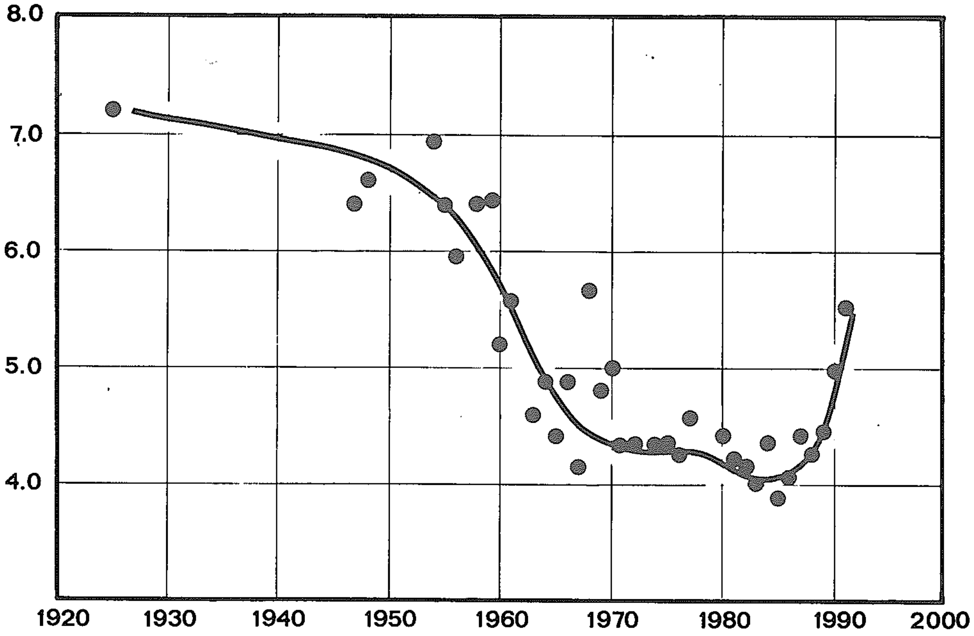

Fig. 8.9. Evolution of mean pH at the overturn.

From March to June 1990 spreading was resumed by spraying the suspension on to the surface of the lake in the maximum depth basin. At the same time as the efficiency of the spreading operation was being monitored, the limnological research, begun in 1984, to evaluate the chemical and biological response of the lake, was continuing.

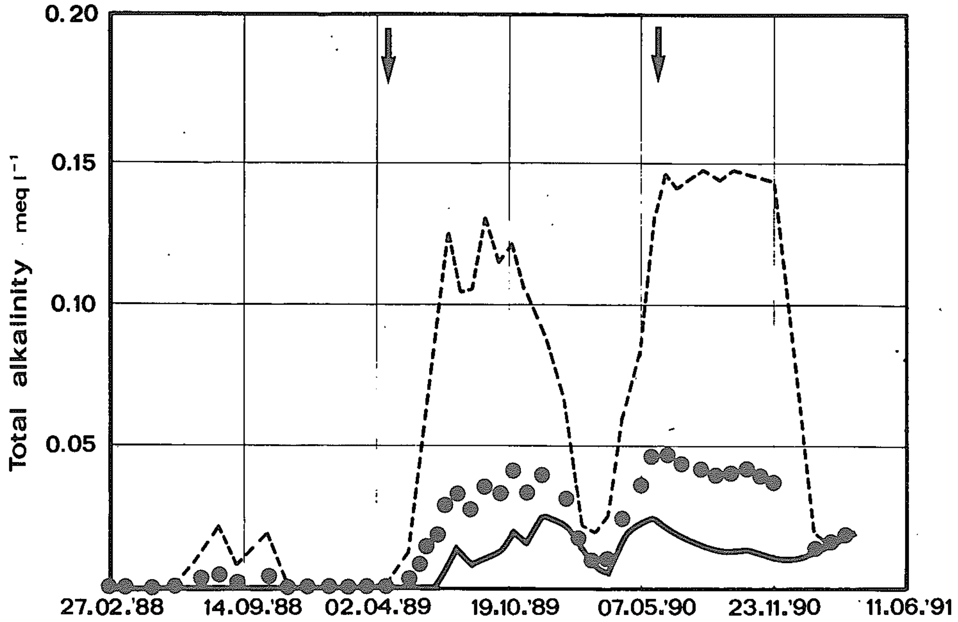

Fig. 6.10. Epilimnetic (broken line), hypolimnetic (full line) and mean total alkalinity (dots) in Lago d'Orta. The arrows indicate the liming period.

6.8 The Effects on Water Chemistry

The most important effects on the lake chemistry after the addition of 14,800 t of natural limestone (the equivalent of 10,900 t of pure $CaC0_3$) concerned essentially the acid-base system (pH, alkalinity and nitrification), as well as the metals most directly responsible for the toxicity of the water (Calderoni et al., 1991).

The effects in general were more striking in the epilimnion, because of the thermal stratification during the summer and autumn period which formed a barrier to the sinking of calcium carbonate in the hypolimnion, as previously discussed. Furthermore during winter 1390, as a consequence of the mild weather conditions, the lake did not present a complete vertical mixing and chemical homogeneization of the water, as normally occurs in this lake in February.

As a result of the buffering effect of the calcium carbonate, pH in the upper 20 m showed peaks up to 8.0-9.0 during summer 1989 and 1990; the periods with pH above 6.0 were of 5 and, months, respectively (Fig. 6.8). In summer 1988, before liming began, and to some extent in the previous years after the Bemberg pollution ceased, there had also been an increase in the pH of the epilimnion due to the input of buffered water from the tributaries; but the values had always been lower than 6.0. The effect of liming on the hypolimnetic water was less pronounced; but at any rate pH did not decrease as a consequence of ammonium oxidation, as observed in previous years. But in winter 1991, when full mixing was reached, a net increase of the mean pH over the whole water mass up to 5.5 was observed (Fig. 6.8); this value is the highest measured for 30 years (Fig. 6.9).

TABLE 6.7.
Volume weighted mean concentrations of the main chemical variables at overturn from 1989 to 1992.

VARIABLES			1989	1990	1991	1992
pH			4.45	4.98	5.52	5.84
Cond. 18 °C	mS	cm^{-1}	112	107	107	106
TA	meq	l^{-1}	0.000	0.005	0.014	0.028
$N\text{-}NH_4$	mg N	l^{-1}	1.21	0.70	0.24	0.09
$N\text{-}NO_3$	mg N	l^{-1}	3.50	3.70	3.80	3.56
TN	mg N	l^{-1}	4.71	4.71	4.44	4.35
RP	mg P	l^{-1}	3	3	1	1
TP	mg P	l^{-1}	4	4	5	5
R Si	mg Si	l^{-1}	4.5	4.2	4.1	3.8
Ca	mg Ca	l^{-1}	9.1	11.2	12.5	12.7
Mg	mg Mg	l^{-1}	1.5	1.6	1.7	1.7
Na	mg Na	l^{-1}	4.9	4.9	1.9	4.7
K	mg K	l^{-1}	1.0	1.0	1.0	1.0
SO_4	mg SO_4	l^{-1}	30.6	31.0	31.4	31.9
Cl	mg Cl	l^{-1}	2.4	2.5	2.4	2.4
Cu	mg Cu	l^{-1}	36	30	26	-
Al	mg Al	l^{-1}	108	86	74	-
Zn	mg Zn	l^{-1}	60	53	40	-
Fe	mg Fe	l^{-1}	77	34	25	-
Mn	mg Mn	l^{-1}	110	147	156	-
Cr	mg Cr	l^{-1}	2	1	1	-
Ni	mg Ni	l^{-1}	16	17	19	-

Total alkalinity, absent in the lake water in the last 30 years, increased during the liming up to 0.1-0.15 meq l^{-1} in the epilimnetic layer, while the mean values for the whole lake reached values close to 0.05 meq

1^{-1} in summer 1990, decreasing to 0.014 meq 1^{-1} at the overturn I991, as a consequence of nitrification (Fig. 6.10 and Table 6.7).

The results of the liming may be best evaluated by considering the variations of the potential alkalinity of the lake, which also express the effect in terms of ammonium decrease. Fig. 6.11 shows the marked increase in the values from - 210 meq 1^{-1} at the 1989 overturn to - 37 meq 1^{-1} at the end of liming (June 1990). Furthermore Fig. 6.11 shows that the recovery of P*Alk* in the lake has taken 1-5 years less than would be the case without liming.

The decrease of potential acidity is largely due to the sharp drop in the mean content of ammonium (Table 6.7), from 1.21 (February 1989) to 0.70 (February 1990) and to 0.24 mg N 1^{-1} (February I991). This was brought about by a resumption of nitrification, which in the preceding years had greatly slowed due to the marked acidity of the lake. In this case, however, the consequent production of hydrogen ion not only tends to cancel out the potential increase in pH deriving from the liming by neutralizing the added bicarbonate, but also, especially in the hypolimnion, is so marked that it acidifies the water below a depth of 50 m to pH values as low as 4.5 units.

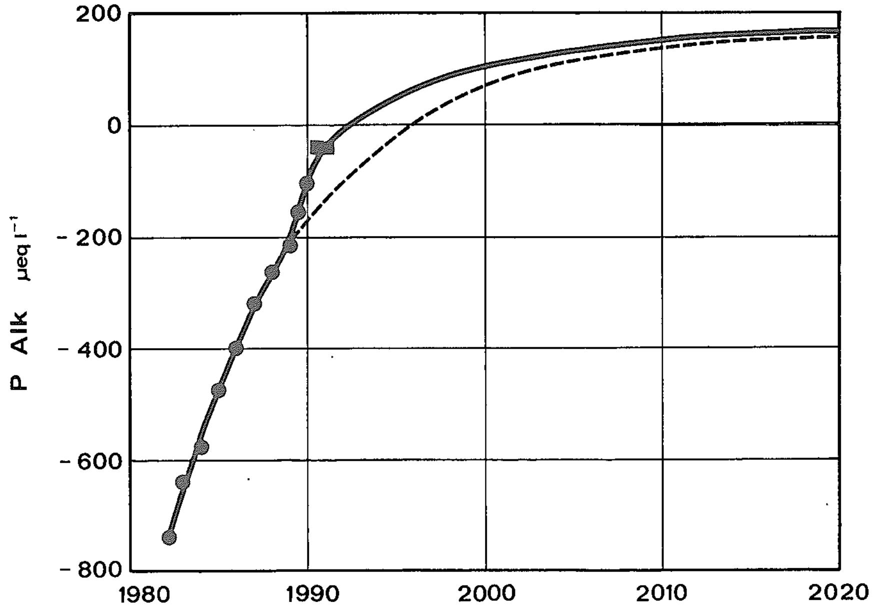

Fig. 6.11 Evolution of P*Alk* following the input-output model (full line), compared with the experimental values at overturn ( ) and in june 1990 ( ). The dotted line indicates the predicted P*Alk*evolution without liming.

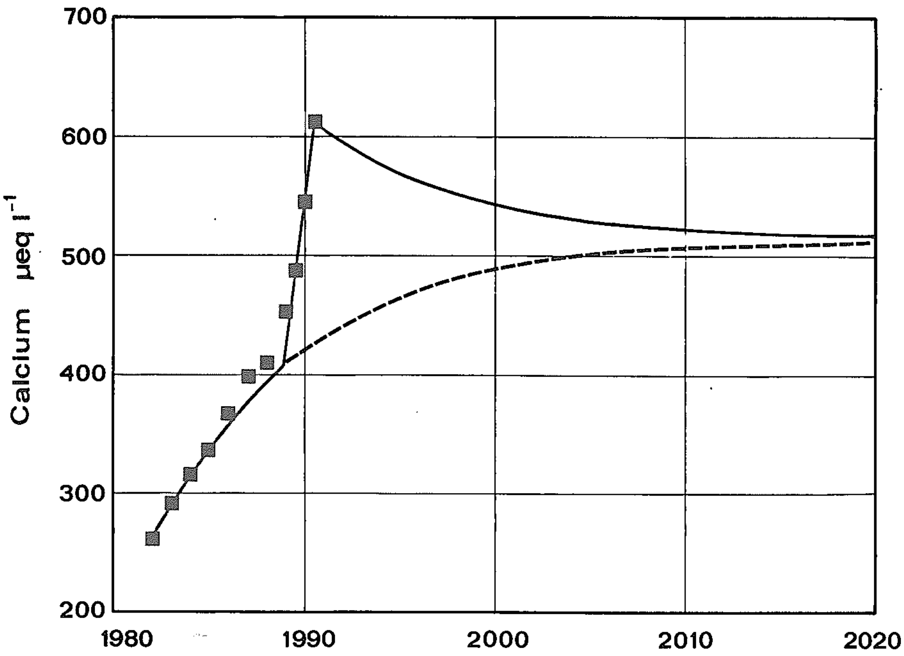

Fig. 6.12 Evolution of calcium concentration following the input-output model (full line), compared with the experimental values at overturn ( ) and in june 1990 ( ). The dotted line indicates the predicted calcium evolution without liming.

Nitrate concentration did not show any marked change, as might be expected from the amount of ammonium oxidized. Indeed the mean concentration in the lake remained close to 3.3 - 3.8 mg N l^{-1} at the overturns of 1989 and 1991 (Table 6.7). The fact that there is no noteworthy increase is probably partly due to the uptake of nitrate from the phytoplankton and the subsequent loss of organic nitrogen due to sedimentation and the output via the outflow both of organic nitrogen and nitrate.

Other major ion concentrations did not show variations subsequent to the liming, with the exception of calcium and, to a lesser extent, of magnesium (Table 6.7). The increase in calcium concentration (Fig. 6.12), calculated from equation (2) with a I_m = 64 meq m^{-3} y^{-1} indicates a mean dissolution of about 85% of the $CaC0_3$ added to the lake.

The response to liming of the concentrations of Cu, Al and Fe (Fig. 6.13, 6.14, and 6.15, respectively) appears to be strongly related to the pH variations, as already observed both in the laboratory experiment and field observation. So the most marked decrease in concentrations took place in the epilimnion, where concentrations lower than 5, 10 and 10 mg 1^{-1} were observed for copper, aluminium and iron, respectively. The decrease of concentration in the hypolimnion was less marked, but the overall effect was a reduction of the concentration over the whole water mass (Table 6.7).

6.9 The Main Changes in Biological Communities

The evolution of biological communities and trophic food webs during the past period of heavy pollution, and the recent ameliorations obtained in the lake are described below.

Due to the copper and ammonium pollution, the phytoplankton communities almost completely disappeared from the lake waters only a few years after 1926 and this situation did not change for at least 30 years. In all that time only a few Clorophiceae, Cyanobacteria species and *Ceratium* sp. were found (Baldi, 1949). It was not until 1956-1957 that there began to be signs of an increase in community complexity, accompanied by the appearance of more abundant populations of the cyanobacteria *Oscillatoria limnetica* (formerly

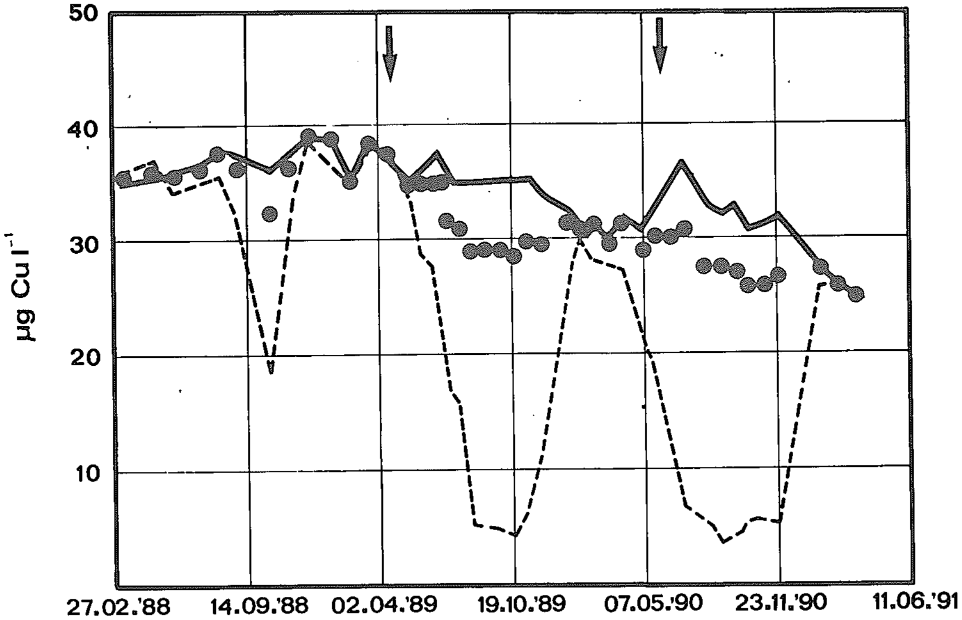

Fig. 6.13. Epilimnetic (broken line), hypolimnetic (full line) and mean copper concentration (dots) in Lago d'Orta. The arrows indicate the liming period.

described as *Lyngbya limnetica*), and of green algae belonging to the genera *Scenedesmus* and *Chlorella* and to the genera *Achnanthes* and *Fragilaria* among diatoms (Corbella et al., 1958; Vollenweider. 1963). At the end of the 60s the green alga *Coccomyxa minor* also appeared in considerable density but at the same time there was a noticeable decline of diatoms (Bonacina, 1970; Vollenweider, 1963). This abnormal situation persisted until the 80s. If we compare the phytoplankton communities before and after 1985, when considerable improvements in pollutant reduction were made, the total phytoplankton density increased, with peaks in production comparable to those observed in mesotrophic lakes; ultraplankton decreased in relative and absolute importance, primarily due to the decline of small-sized cyanobacteria species, not easily identifiable, and of the colonial form *Oscillatoria limnetica*.

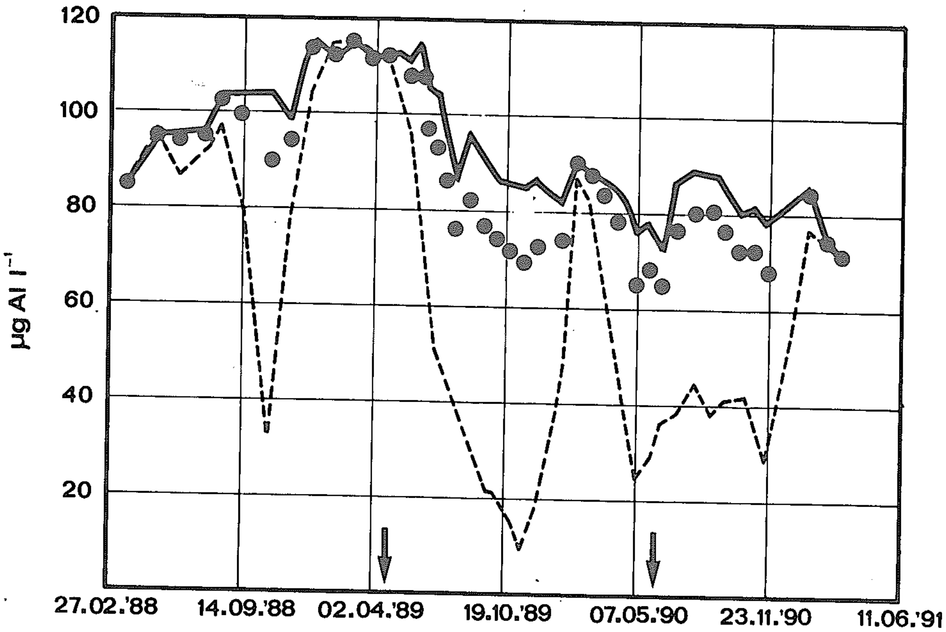

Fig. 6.14. Epilimnetic (broken line), hypolimnetic (full line) and mean aluminium concentration (dots) in Lago d'Orta. The arrows indicate the liming period.

The lake started to assume a phytoplankton structure when green algae began to dominate, particularly with the appearance and increase in density of the genera *Oocystis, Chlamydomonas* and *Scenedesmus*. The diatoms were however still absent or only sporadically found. In general, the community appeared to be dominated by species usually found in highly acid waters, even if the effect of heavy metal concentrations in the water seems to play an important role in structuring phytoplankton community (Ruggiu, D. and G. Morabito, 1990).

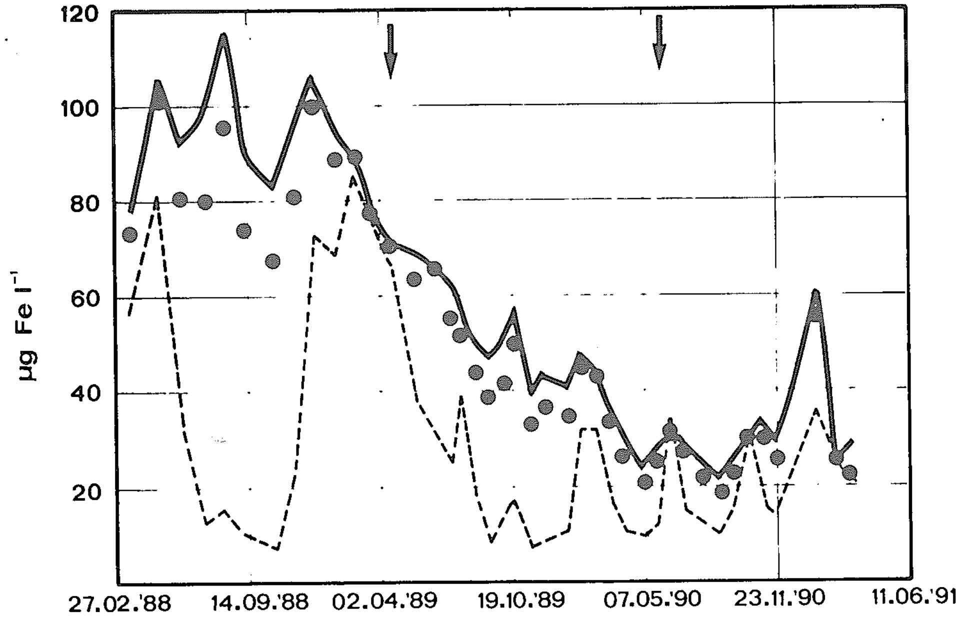

Fig. 6.15. Epilimnetic (broken line), hypolimnetic (full line) and mean iron concentration (dots) in Lago d'Orta. The arrows indicate the liming period.

Before 1926 the lake zooplankton was characterized by a typical community for an oligotrophic lake with the stable presence of 7 cladoceran, 5 copepods and several rotifer species (Pavesi, 1879a, 1879b; Monti, 1930). But only 3 years later, in 1929, almost all the zooplankton disappeared, due to the toxic conditions of the lake water. In the following decades until 1981, the sporadic appearance of *Cyclops strenuus* and a few rotifer species was documented (Baldi, 1949; Vollenweider, 1963; Bonacina, 1970; 1990). Only after the 80s were some specimens of the Cladocerans *Bosmina* sp. and *Chydorus sphaericus* sporadically found (Bonacina, 1990), and after 1986 a small population of *Daphnia obtusa* appeared, which formed a consistently stable population (max density observed 2600 individuals m^3) (Bonacina C. et al, 1988b).

Like the other components of the trophic webs, zoobenthos populations in the profundal area completely disappeared a few years after pollution of the lake began, mainly due to the increase in copper concentration. It was not until the middle of the 80s that recolonization of deep sediments by oligochaetae populations was observed (Bonacina et al., 1988b).

Before pollution, the fish fauna of Lago d'Orta was very rich in species which formed populations of a considerable economic value. In particular. the pelagic waters were inhabited by such species as *Coregonus sp., Alosa fallax lacustris, Alburnus alburnus alborella, Salmo trutta;* the sublittoral zone was characterized by *Salvelinus alpinus, Lota lota* and *Anguilla anguilla,* while in the littoral *Perca fluviatilis, Esox lucius, Cottus gobius, Scardinius erythophthalmus. Leuciscus cephalus, Tinca tinca, Telestes souffia muticellus* and *Barbus barbus* were common.

The annual productivity reached values close to 36 kg ha^{-1} y^{-1} (Tonolli, 1959). Following the worsening of the environmental conditions, by the end of the 80s the most sensitive species had completely disappeared and only a few littoral species (namely: *Perca fluviatilis, Leuciscus cephalus, Anguilla anguilla)* were able to maintain some unstable and reduced populations in limited littoral areas close to the inlets of the small lake tributaries. It is, moreover, important to notice that of these species only *Perca fluviatilis* was able to maintain populations with a sufficient stability; the persistence of the other species was dependent on the early introduction of new specimens (Giussani 1990).

Research during the liming operation highlighted an especially interesting resolution of the algal and animal populations, as regards the rapidity with which the variations, once started, followed one another. in particular, a general increase in the structural complexity of the various communities was observed, with the enrichment of the phytoplankton with new taxonomic entities which had been absent since the very beginning of the pollution. In this connection, the appearance of the diatoms is worthy of note, together with the establishment of a regularity in their seasonal cycles and species succession never observed before.

As regards zooplankton, within a short time permanent populations of Cladocerans of the genus *Daphnia (D. obtusa* and D. *longispina)* appeared, characterized by a good degree of stability; there was also a greater continuity in time of the populations of the copepods previously observed only sporadically, and new appearances in the rotifer community.

In this early stage there has thus already been an increase in the complexity of the food chain in its most significant structural elements, which are indispensible for the attainment of a permanent equilibrium. After liming, there was evidence of the reconstruction of a complete benthos community. Particularly in the littoral areas, almost all the components reappeared with the important exception of molluscs, probably as a consequence of the persistent high copper levels in the sediments.

Finally, at the level of fish fauna, there has not only been an improvement in the structural conditions of the populations of littoral species, especially the perch (*Perca fluviatilis)* due to its better reproductive success, but there has also been a reappearance, albeit in very low density of *Alburnus alburnus alborella*, a pelago-littoral planktivorous species not found in the lake for over 50 years. In addition, species such as *Coregonus sp., Salvelinus alpina, Salmo trutta, Anguilla anguilla,* which differ greatly in their sensitivity to the various pollutants, have been successfully introduced.

6.10 Conclusions

The results obtained so far confirm that the liming is bringing about positive changes in the lake chemistry and is also contributing to the re-establishment of a structurally more complex biological community. It is therefore essential to continue the operation until the permanent recovery of the lake is guaranteed.

The mean value of the potential alkalinity, found at the overturn 1992, was 14 meq m^{-3} (Table 6.7). On the basis of the numerous studies performed in the last ten years, it may be said that the minimum objective in terms of alkalinity is an in-lake mean value of at least 100 meq m^{-3}, which corresponds roughly to 50% of the original natural value. This means that the total negative balance is 86 meq m^{-3}.

Assuming that the input to the lake of bicarbonate and ammonium remains of the same magnitude as in recent years (27 Meq y^{-1} of positive P*Alk*), then using the proposed model, it can be estimated that another 5,600 t of pure $CaC0_3$, the equivalent of about 10.000 t of the limestone used, will have to be added to the lake to guarantee the attainment of the objective proposed, if a prudential dissolution efficiency of 75% is assumed.

It is estimated that the additional liming can be completed in months. After the complete oxidation of the ammonium still present, which will take 1-2 years, the lake will conserve its alkalinity, as the results clearly demonstrate that the load of bicarbonate from the tributaries is sufficient to maintain a lake salinity of about 0,2 meq 1^{-1} once reached the equilibrium. Furthermore, the increased pH will drastically reduce the trace metal concentrations. The chemical recovery will thus be definitive, allowing the lake to reach in a few years a more balanced and stable biological situation.

Acknowledgment

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CHAPTER 7

SHALLOW LAKES AND THE INFLUENCE OF ACID RAIN ON THEIR WETLANDS AND SHORE VEGETATION

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Denmark

7.1 Introduction

The small volume of water in shallow lakes explains the sensitivity towards environmental pollution of many shallow lake types. The occurrence of low buffering capacity and a small nutrient supply, e.g., with respect to nitrogen, renders the water body very sensitive to environmental changes such as acidification and eutrophication. These phenomena are both believed to be of crucial importance in connection with the overall destabilization of many natural, North European ecosystems, including shallow lakes, their shore vegetation, ombrotrophic mires, etc.

The shore vegetation surrounding the shallow lakes may be regarded as a protective transition zone between the lake itself and the landscape in which the lake is situated; see also Guideline Book number three on Lake Shore Management. A stable, ecologically well-developed shore vegetation may be able to absorb an appreciable part of compounds otherwise bound for the open water body. This fact is due to the composition of the shore vegetation and its biological, physical and chemical properties. In the case of most shallow lakes on sandy soil, the shore vegetation will be poor, i.e., dominated by bryophytes, in particular *Sphagnum* spp. These plants retain water efficiently and prevent any horizontal water flow from the surroundings to the lake. Furthermore, they are cationexchangers able to exchange ions such as sodium, potassium, calcium, magnesium ions with hydrogen ions.

Changes in the surrounding environment with respect to agricultural practice and the atmospheric deposition of pollutants may, however, reduce the stability of the shore vegetation leaving the lake far more open to adverse impacts. Acidification is due mainly to deposition of oxidized sulfur and nitrogen compounds. The sulfur compounds may disturb Sphagnum - vegetation, as shown in the English Midlands. The levels of sulfur deposition were, however, much higher than today; in most of the Northern Europe, the deposition of sulfur-dioxide and sulfate itself is probably of insignificant importance with respect to destabilization of fens and bogs observed. The increasing supply of hydrogen ions may cause destability.

It is necessary to underline, that pH in the free water between Sphagnum plant's cavity may fall below 3; the current level of pH in precipitation in Denmark is about 4.2. Eutrophication in a broad sense and depositions of nitrogen compounds from the atmosphere in particular, are the main threats to most shallow lakes in sandy, nutrient poor areas and to their shore vegetations of fens, mires and bogs. Changes in the vegetation have already been observed, minerotrophic species of Sphagnum replacing the original plants in dynamic equilibrium with the oligotrophic conditions invade the fens, mires and bogs. This chapter deals with case studies reflecting these points.

7.2 Nature Types and Ecosystems

The term "nature type" is rather wide, mostly used for areas, places or small spots, considered to be in a more natural state, that is, less affected by man, than the rest of our environment. The term is used here for a wide range of areas, where a number of naturally occurring species of plants and animals live and reproduce.

Wild plants and animals are interrelated in various ways, animals eating plants or other animals, etc. These relations can be described or depicted in an ecosystem. In one sense, all living creatures belong to one global ecosystem. However, this is normally not a practical unit to handle, and is broken down into smaller units, corresponding to the nature type or site, one wishes to describe.

An ecosystem can be simple or complex and can contain a varied number of species and individuals. Therefore, the possible variation in ecosystems is large. The ecosystems will always develop toward a climax state. Varied ecosystems offer more different places to live for wild animals and plants (habitats), ensuring a variation in the number of species, that can live in our environment.

Certain climax ecosystems are very susceptible to changes in environmental factors affecting them and easily brought out of balance. Man-induced factors are often the most disastrous, since they are often irreversible, restricting the ecosystem's possibilities of returning to the climax state. In our part of the world, a relatively small number of climax ecosystems are found. Many have been disturbed thoroughly by man over the last 2-3000 years, since the agrarian expanse started, and destruction has accelerated after the industrial revolution, leaving few "intact" ecosystems.

7.3 Wetlands

Wetlands may be considered as one of these intact climax ecosystems / nature types. They are dependent on rainwater. Over the last few decades many wetlands have become affected by drainage, often a result of drainage of adjacent farmland.

A more recent impact on wetlands is air pollution, which now affects most ecosystems on Earth. Air pollution affects ecosystems through injury to sensitive species of the system and /or through change in their nutrient cycling and supply. It may take long before improvements in the ecosystem's health is seen following emission control measures.

Wetlands are particularly sensitive. Some are characterized by low content in nutrients, especially nitrogen, which is now being supplied in large amounts by the deposition of atmospheric nitrogen compounds. Intact wetlands are becoming very scarce in the more densely populated parts of Europe, and much effort is now being put into their rescue by conservation authorities and concerned societies. Our sensitive ecosystems are lichen-rich communities, which are sensitive to sulfur-dioxide, but also to fertilization, altering the flora composition (Johnsen and Søchting, 1973 and Fiskesjø and Ingeløg, 1985). As a result of the emission of sulfur-dioxide, these communities will change into less species-rich ones or disappear completely. This leads to a decrease in variation, which is not considered desirable. Streams and lakes on acid bedrock are also particularly sensitive ecosystems (Hutchinson and Havas, 1980). Some ecosystems are thought to be more robust to sulfur-dioxide emission and the acid rain resulting from it, for example lakes situated in chalk grassland, which can buffer the acidity. But even here signs of degradation are beginning to show (Tregenza, 1986).

7.4 Vulnerable Ecosystems

Some typical examples of vulnerable ecosystems belong to the following groups:

- natural and climax ecosystems. Man's role is small but time has shown that this will, unfortunately, not continue.

- simple ecosystems. Extinction or invasion of one or a few species can easily make the system collapse and

-systems subject to recent human influence (e.g. drainage) and still possessing the main original qualities

Our future environment will contain less wild species of plants and animals - for various reasons. Compared to the last, say 300 years, direct pursuit of the single species will account for a still smaller proportion of the extinction rate. Direct destruction of habitats and ecosystems will still have a large share and will probably increase. But it is also thought that the overall deterioration of the global environment, mainly pollution of the atmosphere and the oceans, will account for a larger share. Unfortunately, the connection between the diffuse pollution and the general impoverishment of our environment is less obvious to the layman than is the simple relation between decrease of Fen Orchids and drainage and cultivation of meadows where they used to grow.

7.5 Sulfur Deposition

Sulfur as an air pollutant originates predominantly from burning of coal and heavy fuel oil. It is emitted as sulfur-dioxide but is soon oxidized in the atmosphere to sulfuric acid, which dissociates into two hydrogen ions and sulfate. The ratio sulfur-dioxide to sulfate is the air will therefore indicate, if the sulfur is of relatively local origin or comes from more remote sources; see Figure 1. At many EMEP-station (NILU, 1986), both fractions are measured.

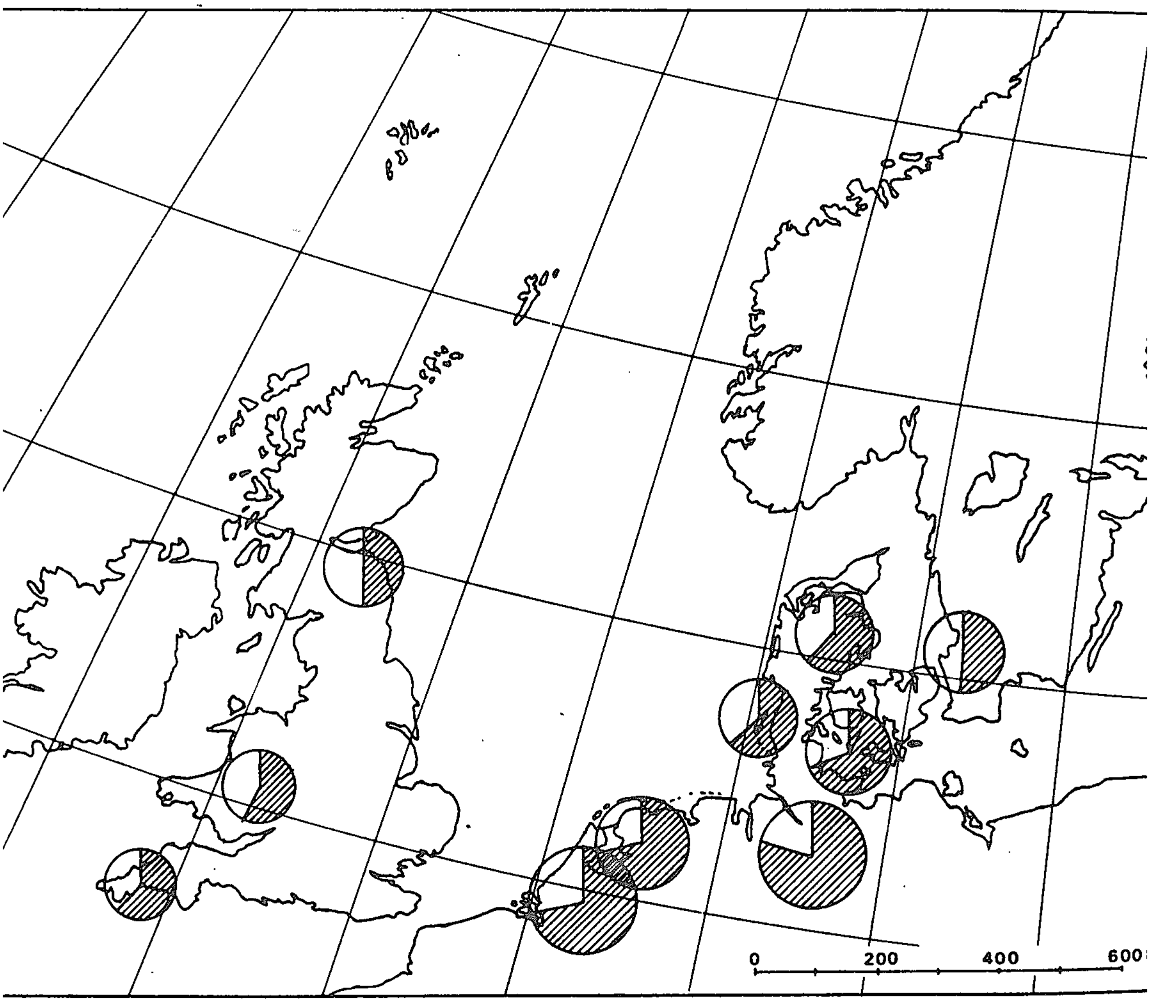

Fig. 7.1 Relative total and dry deposition (hatched) of sulfur, yearly average, period 1978-85. Diameter proportional to deposition. Data supplied by NILU, 1986.

Sulfur will be deposited as sulfate in rain and in droplets (wet deposition) or particles, suspended in the air and as the gas sulfur-dioxide (dry deposition). The dry deposited sulfur is often measured together with the wet deposition, when particles settle on the sampling device (bulk sampler). Fowler (1980) quotes ratios for dry versus wet deposition of sulfur from 8-12 close to larger pollution sources, to < 1 in areas more than 300 km from larger sources. Since vegetation of a wetland has a much larger exposed surface (leaves) per area unit than the sampling device and gases can be directly assimilated by the plants, the uptake values (deposition + assimilation) might well be larger than the measured values indicate.

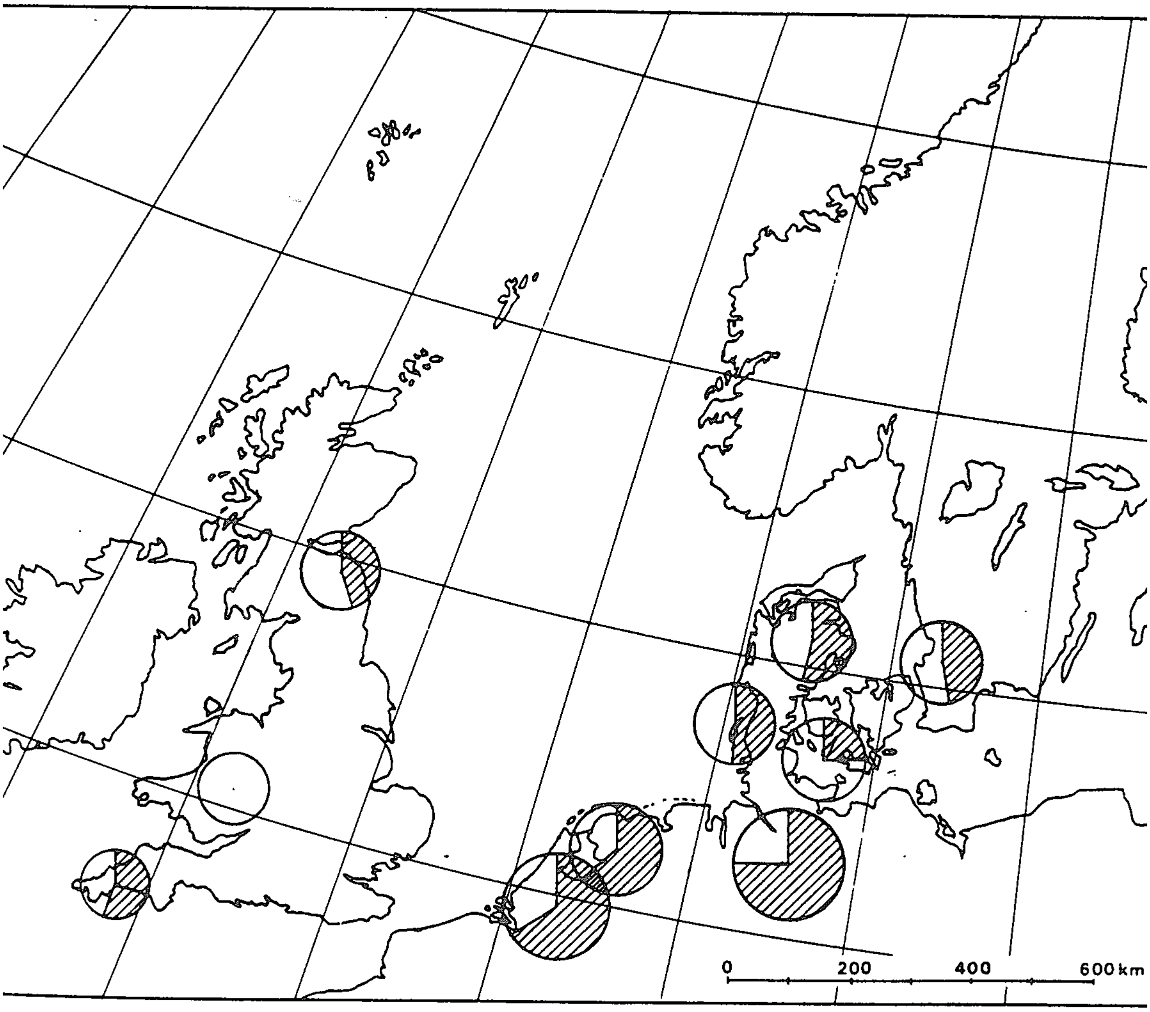

Fig. 7.2 Total deposition of sulfur and sulfur-dioxide in percentage of the total deposition (hatched), average for the period 1978-85. Data supplied by NILU, 1986.

Droplets in the atmosphere, containing sulfate can also originate from sea spray - a station close to the sea. This can account for 50-80% of the sulfate measured. Correction for this fraction is possible, using measured chloride concentrations.

Preliminary data on the most recent deposition measurements at relevant EMEP stations were supplied by the Norwegian Institute for Air Research (NILU). Data from the period 1978-85 were used. In a few cases, estimates on dry deposition, especially nitrogen, had to be made from other sources (Hutchinson and Havas, 1980 and Miljøstyrelsen, 1984) to get a total picture of the deposition.

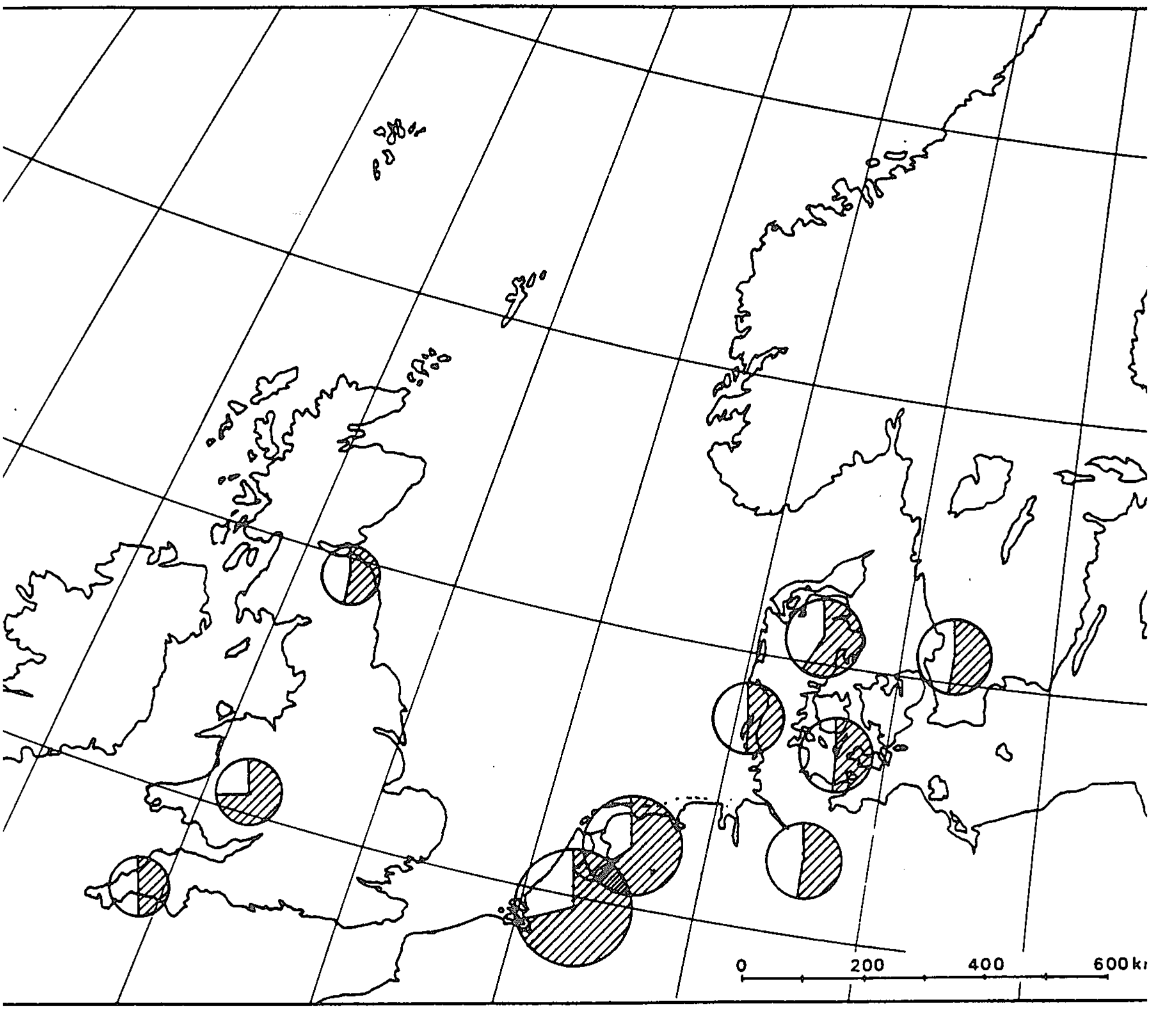

Fig. 7.3 Total deposition and dry deposition (hatched) of nitrogen, relative values, yearly averages, period 1978-85. Data from NILU, 1986.

Dry deposition was calculated from the relevant gas concentration means. Total deposition is presented here as wet deposition plus calculated dry deposition. This gave higher values, since wet deposition in some cases was given as bulk sampler results. These last were corrected for sea spray in the case of sulfur, giving total sulfur amounts deposited between 740 g/ m^2/ year for the West Irish station and 3999 g/ m^2/ year for the Mid-Netherland station.

7.6 Nitrogen Deposition

Nitrogen as a pollutant is found in the atmosphere as oxides of nitrogen (mainly NO and NO_2), originating from combustion of fuels and as ammonia, mostly from heavily fertilized fields. Both wet deposition and concentrations of the particulate and gaseous fractions are measured at some EMEP stations, and then only for the last few years, The dry deposition rates on vegetation are difficult to assess, since the vegetation normally is in shortage of nitrogen, and readily take up atmospheric nitrogen compounds. The values for total nitrogen deposition vary from 1000 mg/ m^2/ year for the Southern and Northern British stations to 4381 mg/ m^2/ year for the Mid Netherland station. There are no data from the Irish station. Amounts are presented relatively in Figure 7.3.

7.7 Effects of Air Pollution

Damages due to pollution are difficult to assess, since only little is known about the tolerance of the various species to low pollution loads. The lack of lichens in the analysis from Langeveen (a dutch wetland) and the poor species variations in some Danish wetlands are remarkable. Licehns are known to be particularly sensitive to sulfur-dioxide (Johnsen and Søchting, 1973). The compound is quickly oxidized to the much less harmful sulfuric acid.

Short term exposure to sulfur-dioxide concentrations of the same order of magnitude as those measured at some EMEP stations has a selective effect on Sphagnum species (Ferguson, Lee and Bell, 1978), reducing growth of typical wetland species like *Spagnum tenellum* and *Spagnum imbricatum* much more than *Sphagnum magellanicum* and *Sphagnum fallax.*

A large number of Sphagnum species was found in the least polluted Danish wetlands, which indicates that the number of species in wetlands may be used as an ecological indicator.

The magnitude of nitrogen deposition influences the Sphagnum species composition of wetlands. The fen species *Sphagnum fallax* has a higher nitrogen content than *Sphagnum rubellum, Sphagnum tenellum* and *Sphagnum papillosum* (Slater, 1974, and Pakarinen and Tolonen, 1977) and grows much faster (Pedersen, 19759. *Sphagnum fallax* may require more nitrogen, which in nature is mainly supplied from water. These species may grow faster and outcompete especially *Sphagnum rubellum* and *Sphagnum subnitendls*, which occupy approximately the same microhabitat in the hummock-hollow system (Pedersen, 1975, and Anderson, 1986). This will then change the species composition away from the natural species spectrum in the wetlands. Detailed investigations of the reaction of the wetlands' plants, especially Sphagnum, to oxides of nitrogen and ammonia have not been found in literature.

Negative effects from air pollution will add to the negative effects of drainage.

7.8 Chemical Analysis of Vegetation

The contents of nitrogen vary between 0.49% in the basis of Sphagnum from the wetlands with smallest deposition estimates, to 1.42% in wetlands with the highest estimated deposition. The West Irish blanket bogs are thought to represent the background, natural state of Sphagnum plants. The nitrogen content in the Sphagnum apex in the most polluted wetlands in Denmark is about twice that of the background samples.

In all wetlands investigated nitrogen content in Sphagnum apex is higher than in basis, indicating a recycling of the nitrogen (Polett, 1972 and Hemond, 1983). There are substantial differences between the estimated relatively unpolluted wetlands and those receiving higher depositions. The difference is significant to the 0.5% level in both Sphagnum fractions, whereas the content in the fanerogams is not significantly different.

The observed contents of nitrogen in plant material were compared to the estimated deposition of nitrogen, and the probability of positive correlation was

91% for Sphagnum apex and 86% for averages of all plant fractions. Provided the estimates are reasonably good, this means that Sphagnum can be used as indicators for air pollution. The higher plants are less affected, relying on root uptake.

Material from Irish blanket bogs revealed the lowest nitrogen content, indicating a background level, although direct comparison to raised bogs is not possible. The samples in the blanket bogs were taken under conditions very similar to that of the other samples.

Samples of the lichen, *Cladina portentosa*, collected in the Irish bogs, revealed a content of 0.26 -0.58% total nitrogen. Samples from polluted areas showed a significant higher nitrogen concentration in the order of 1%.

For total sulfur , the contents vary between 0.107 - 0.373 in plant material and 0.25-0.65 in peat samples. Values of 0.1-0.2% total sulfur for fanerogams have been reported from South Sweden (Malmer and Sjørs, 1955) and approximately 0.05% for Northern Sweden) Malmer and Nihlgård, 1980) For *Sphagnum fuscum* and *Sphagnum balticum* in Finland, concentrations of 0.12-0.14% have been reported and for basis of 0.102% (Pakarinen, 1981a).

For Sphagnum apex, the concentration increase from background values (West Irish blanket bog) to the polluted Danish wetlands is 50%. The differences observed are probably due to higher dry and wet deposition of sulfur on the continental wetlands.

Statistical probability of correlation with estimated deposition of sulfur is 96%; which is better than the correlation for nitrogen. The correlation in the other fractions is not clear, an average for the sulfur content in apex, basis and fanerogams gives a probability of positive correlation of 69%. In Finland , Parkarinen (1981b) found correlation between sulfur deposition and sulfur content in *Sphagnum fuscum* and *Cladonia arbuscula.*

Concentrations in peat and plant material are low in the Swedish localities. This could indicate actual low deposition and the estimates, which are based on values from an EMEP station some 150 km to the Southwest, are probably high. Therefore, as in the case of nitrogen, Sphagnum seem to be very good indicators for sulfur deposition.

Sphagnum are good indicators of total depositions of heavy metals from the atmosphere, which accumulate in the plants (Aaby , 1986, and Wandtner, 1981). This accumulation is not believed to affect the plants directly and will therefore not affect the vegetation composition. *Sphagnum recurvum* has been shown to indicate aerial fluoride pollution (Swieboda and Kalemba, 1981).

7.9 Cations, pH and Conductivity

The amounts of exchangeable ammonia in peat and water samples are all very small, and often close to detection limit. There is a tendency to significantly higher levels in the most polluted wetlands. In Danish wetlands, effects from farmland might account for the difference. The amounts found and the number of analyses do not allow a firm conclusion.

The amount of exchangeable calcium and magnesium are highest in the oceanic localities. The amounts are measured on fresh samples and corrected back to the dry weight to get a picture of the plant accessible cations and are not directly comparable to values in other papers, where extraction was made on dried samples (Pollett, 1972 and Waughman, 1980).

According to several authors, referred to in Waughman, 1980, a calcium: magnesium ratio about 1:1 should indicate ombrotrophy and the ratios found in the wetlands are also close to this value. The Danish wetland Holmegård has the highest ratio, indicating some degree of influence from groundwater, although most samples were taken in the center of the wetland, over more than 1 m peat. It is concluded that in the case of cations extracted from fresh peat, the Ca:Mg ratio indicates the degree of ombrotrophy, when comparing the wetlands mutually.

The aluminum contents vary very much - and the variation in samples from each wetland is even larger than the variation between the averages. The high average values from some wetlands and the variation in samples from the same wetland might be part of the explanation for dead Sphagnum patches, observed in several wetlands. An explanation for this variation cannot be given.

Acidity of wetland water is particularly low in the Swedish wetlands. Some of the water samples have high conductivity, indicating a high ion content. Calcium ions varied between 0.1 meq / l to 0.3 meq / l. Potassium ions varied between 0.03

and 0.04 meq / l in all wetlands, with no clear tendency in differences. Magnesium concentrations were about 0.15 meq / for all wetlands, apart from extreme oceanic localities, where concentrations were 2 meq / l.

7.10 Main Conclusions

The observed differences in vegetation in the wetlands can be correlated to estimates of deposition of nitrogen and sulfur.

Comparison to available older descriptions revealed changes, which could primarily be ascribed to drainage. The present vegetation analyses revealed differences between the wetlands, some of which could be attributed to differences in deposition of sulfur and nitrogen, others to drainage.

High deposition values for sulfur dioxide seemed to cause reduced plant diversity with a complete lack of lichens in the most polluted ones. Some changes in the vegetation composition, such as decrease in typical wetland species, may be caused by high deposition of nitrogen compounds.

The chemical analyses of plant material showed statistically significant differences in the content of both nitrogen and sulfur, when compared to a defined "clean" reference wetland. In particularly, the contents of Sphagnum species were positively correlated to estimates of depositions of nitrogen and sulfur.

Exchangeable ammonium was present in small amounts in the examined wetlands, especially in wetland water. There was a trend towards higher values in more polluted wetlands, which may lead to changes in the fanerogam flora. Ratios of calcium to magnesium are between 0.69 and 2.21.

Low total nitrogen contents in the lichen *Cladina portentosa* and Sphagnum were found in the West Irish Blanket Bog.

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CHAPTER 8

ACIDIFICATION OF LAKES IN CANADA

extracted from Government of Canada, The State of Canada's Environment 1991

8.1 Introduction

Since the mid-1970s, extensive and intensive research has been conducted in Canada to define aquatic effects associated with elevated acidic deposition. This paper provides an overview of the "acid rain" story in Canada -- the condition of Canadian aquatic resources as influenced by the long-range transport of air pollutants.

8.2 Background

During the 1980s, "acid rain" became, for many Canadians, a definitive symbol of environmental crisis. In the early 1980s, the "war" against acid rain was largely waged on fronts such as deteriorating water quality and diminishing fish populations. The acidification of supposedly pristine lakes in the Canadian Shield, a 4 million square kilometre area of Canada characterized by bare rock and thin soils, offered an arresting image. Despite the fact that acidic deposition affects more than lakes, the image of the biological death of lakes in remote wilderness was a useful focal point for garnering public support for the complex task of negotiating emission standards and other corrective measures.

In Canada, acidic deposition was not identified as an environmental concern until the 1950s. Working at Dalhousie University in 1955, Dr. Eville Gorham attributed the "abnormal acidity" that he detected in precipitation, and in the water of Nova Scotia lakes, to airborne pollutants which, he theorized, might come from distant sources. Surface water surveys and monitoring that had been undertaken by the Canada Department of Mines and Technical Surveys (Thomas 1953) provide a valuable baseline for early documentation of the trends and consequences of acidification.

In 1966, Dr. Harold Harvey, at the University of Toronto, detected severe losses among fish populations in the lakes of the La Cloche Mountains, southwest of Sudbury, Ontario, and ascribed these losses to acidification of the waters by acid rain (Beamish and Harvey 1972). Two large research programs, the International Joint Commission's reference reports on the upper Great Lakes (International Joint Commission 1982) and the Sudbury Environmental Study undertaken by the Ontario ministries of Environment and Natural Resources (Ontario Ministry of the Environment 1979), both produced reports that identified this state of abnormal chemistry in precipitation falling on Ontario lands and waters.

Such research findings, backed by others from abroad, prompted the convening of a symposium in 1975 to address the "Atmospheric Contribution to the Chemistry of Lake Waters" (Matheson and Elder 1976). In May 1976, Environment Canada directed the formation of a committee of scientists to study the long-range transport of airborne pollutants (LRTAP). The report of this group (Whelpdale 1976) stated that:

> "In Canada, the potential for problems of this nature exists. We have the meteorological conditions which are conducive to transport from source regions in Canada and the United States to regions of the country which have sensitive soils, waters, fish and forests."

8.3 Sources and Deposition of Acidic Pollutants

Although natural sources of sulphur oxides and nitrogen oxides do exist, more than 90% of the sulphur and 95% of the nitrogen emissions occurring in eastern North America are of human-made origin. The largest sources of these pollutants are the smelting or refining of sulphur-bearing metal ores and the burning of fossil fuels for energy. In 1985, about 70% of the sulphur dioxide emissions in the United States came from coal-or oil-fired electrical generating stations; in Canada, about 50% was emitted from ore smelters and about 20% from generating stations burning fossil fuels. Sulphur emissions in both countries tend to be concentrated in a relatively few locations. By contrast, the sources of nitrogen emissions are widely distributed. About

40% of nitrogen oxides come from transportation (cars, trucks, buses, trains), about 25% from thermoelectric generating stations, and the balance from other industrial, commercial, and residential combustion processes.

Figures 1 and 2 show the distribution of North American sources of sulphur oxides and nitrogen oxides and the levels in the geographical areas delineated on the map. In 1980, which has served as the reference year for tracking emissions, sulphur dioxide emissions were estimated to be 4.6 million tonnes in Canada, and 24 million tonnes in the United States. Emissions of nitrogen oxides in the two countries were 1.8 million and 20 million tonnes, respectively. Figure 3 shows trends for sulphur dioxide emissions in eastern Canada and in Canada as a whole, along with 1994 emission control objectives for eastern Canada.

In eastern North America, weather patterns generally travel from southwest to northeast. Thus, pollutants emitted from sources in the industrial heartland of the midwestern states and central Canada regularly fall on the more rural and comparatively pristine areas of the of the northeastern United States and southeastern Canada. Figure 4 shows the annual rate of sulphate deposition across North America in 1980. It is evident that southern Ontario and southwestern Quebec received the greatest amounts. (The average pH of precipitation in central Ontario is about 4.2 [RMCC 1990, part 3].) A continental network of weather stations has been monitoring acidic deposition since about 1979, long enough to indicate changes or trends that have occurred over the past decade. Sulphate deposition in precipitation, though still at undesirable levels in many parts of eastern Canada, has declined at an approximately steady rate (see Figure 5).

The capacity of any region to neutralize acidity is determined primarily by the characteristics of its soils and bedrock (Cowell and Lucas 1986). A model based on available information from terrain, soil, and ecological land inventories ranks Canadian landscapes in three sensitivity classes - high, moderate and low - with regard to their potential to withstand acidic deposition (Figure 6). A large proportion of the landscapes

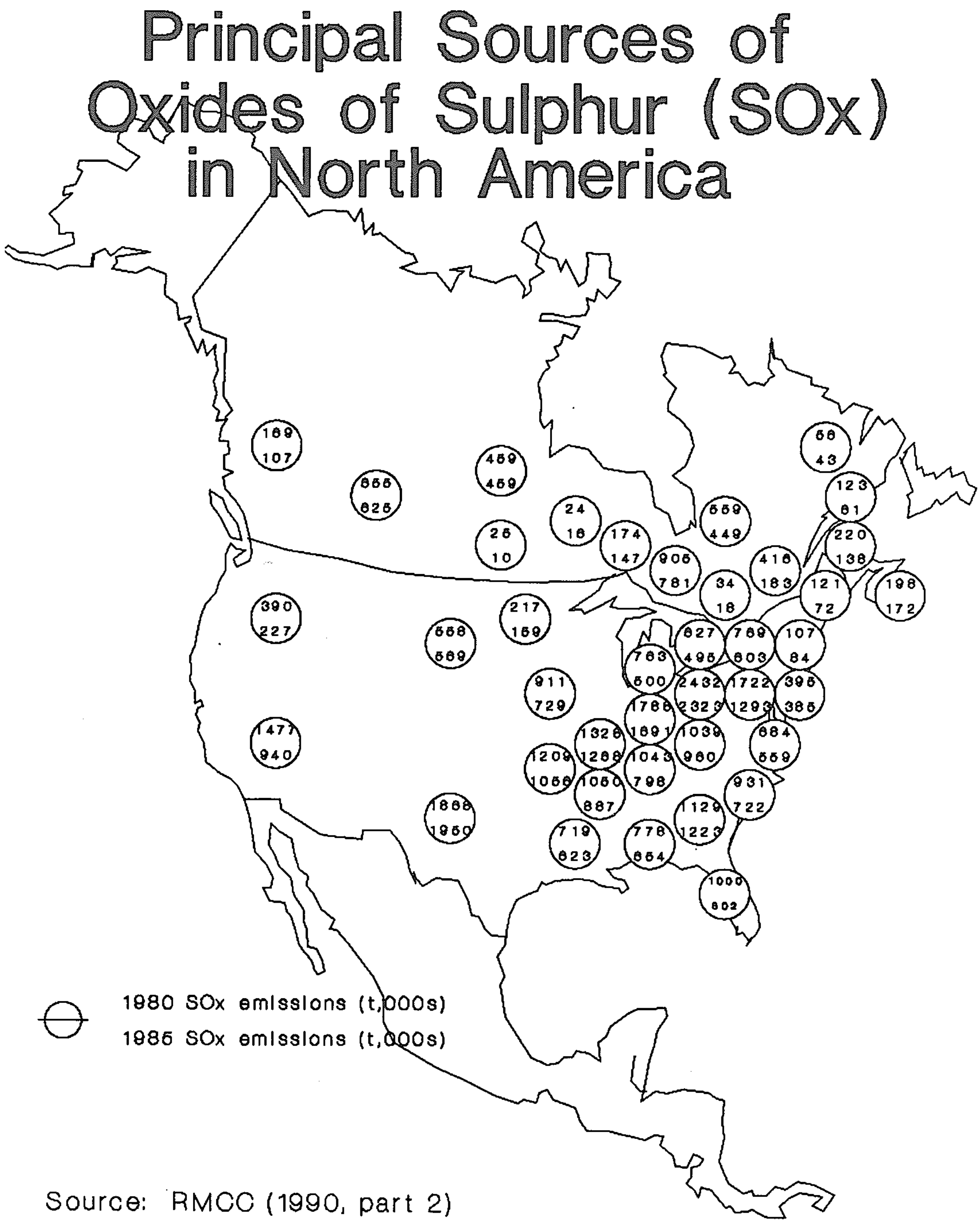
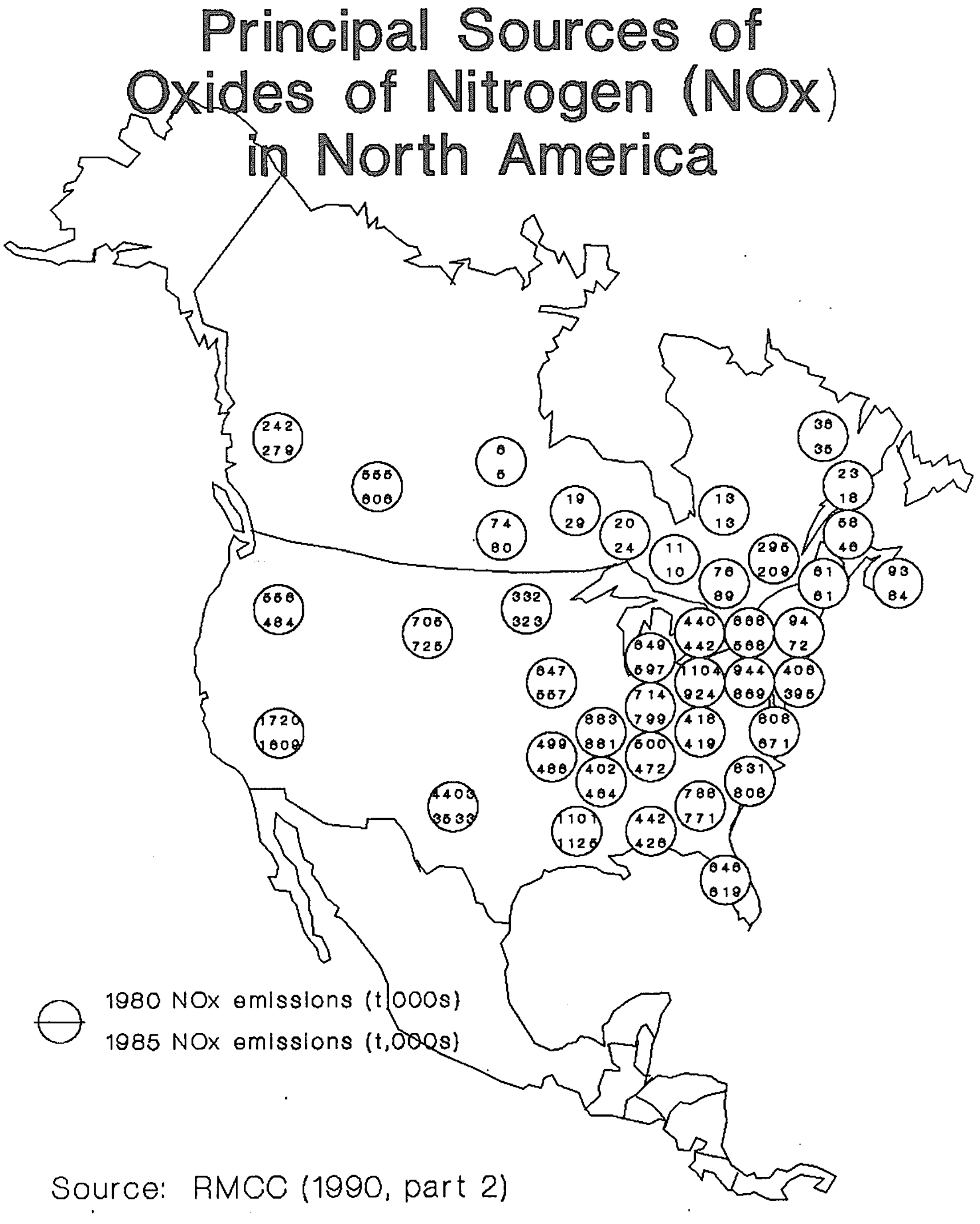
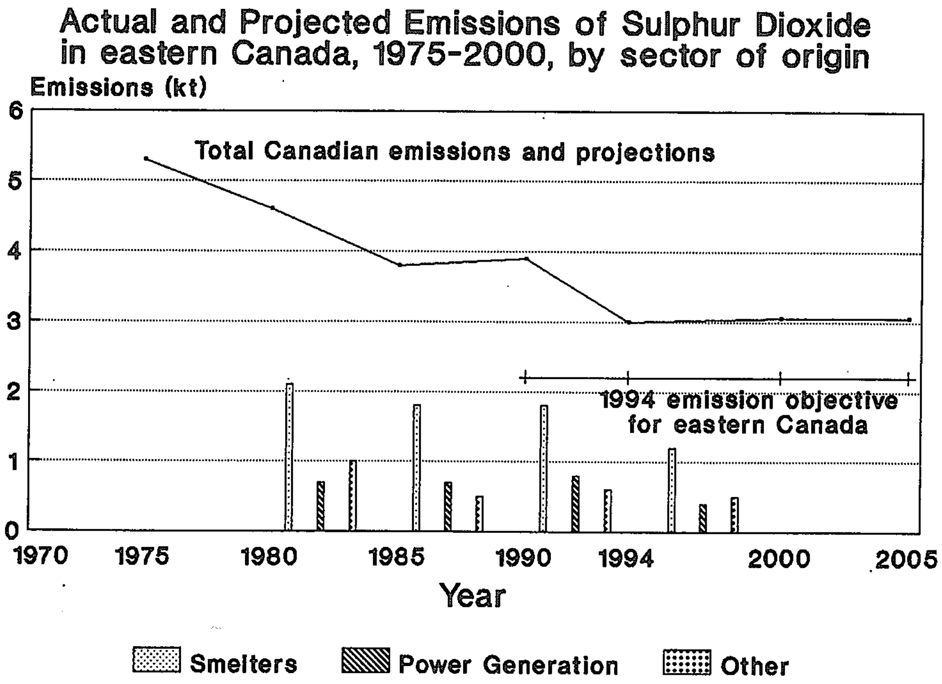


Fig. 1. Distribution of North American sources of sulfur dioxide.



Source: RMCC (1990, part 2)

Fig. 2. Distribution of North American sources of nitrogen oxide.



Source: RMCC (1990, part 2)

Fig. 3. Actual and projected emissions of sulfur dioxide in Eastern Canada, 1975-2000, by sector of origin.

with low capacity for reducing acidity, and thus with high sensitivity, lie in the Canadian Shield, an area dominated by granitic bedrock and thin, poorly developed soils. This area contains a large proportion of Canada's wealth of lakes and wetlands, in all about 4 million square kilometres, about 46% of Canada's surface area.

Clearly, the occurrence of high levels of acidic deposition in regions with low neutralizing capacity is most likely to seriously damage ecosystems. By comparing the areas with high levels of wet sulphate (sulphate measured in precipitation) deposition (Figure 4) and the areas of high sensitivity (Figure 6), it is easy to see where the two conditions coincide. In 1980, more than 10 kilograms per hectare of sulphate were deposited over sensitive landscapes in Ontario, Quebec, the Atlantic provinces, and, to a lesser extent, southwestern British Columbia (not shown in Figure 4). Significant, and in some cases severe, ecological response to acidic deposition, in the form of damage to lakes, are found in these regions.

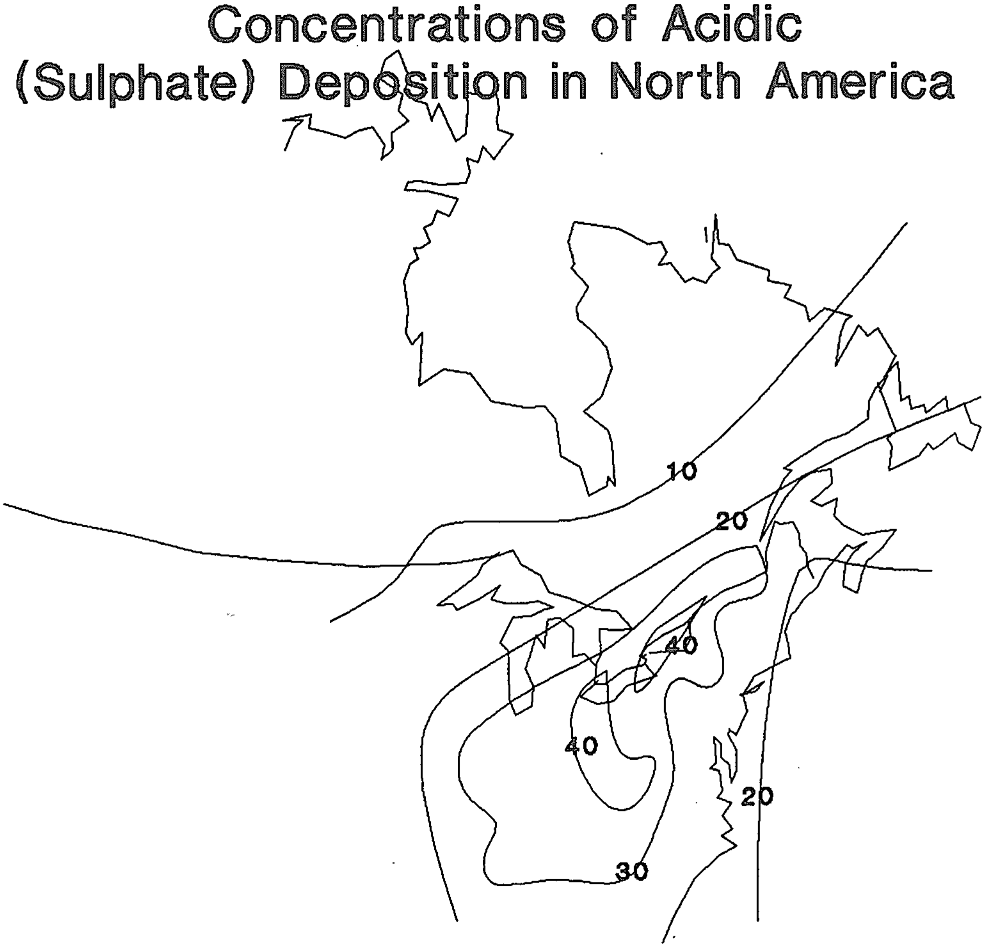


Fig. 4. Concentrations of Acidic (sulfate) deposition in North America.

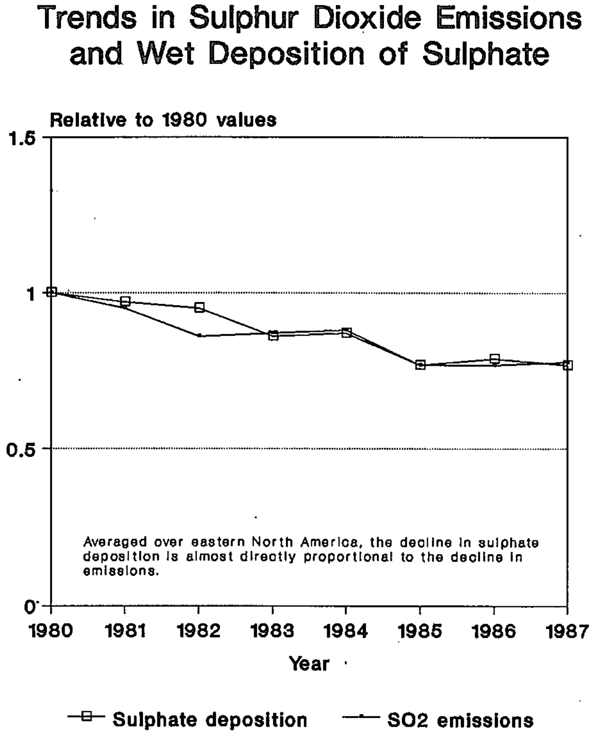
The numbers represent concentrations of acidic (sulfate) deposition expressed in kilograms of sulfate per hectare per year. The lines outline areas that accumulate more than 10, 20, 30 and 40 kg/ha in a year.

Note: Eleveated levels of sulfate deposition in parts of Alberta and Saskatchewan are due to the presence of calcium sulfate in wind-blown, nonacidic soil (RMCC 1990, part 3).

Source: Barrle and Hales (1984).

8.4 Aquatic Response to Acidic Pollutants

Canada has a wealth of fresh water. Lakes, streams, and wetlands cover about 7.6% of Canada's surface area, and the volume of groundwater is many times greater than the volume of surface water. Recently, a satellite study of water bodies (Hélie and Wickware 1990) was conducted for the region of Canada that is most affected by acidic pollution, that is, the area east of the Manitoba - Ontario border and south of 52° north latitude (Figure 7). In this region more than 775,000 water bodies larger than 0.18 ha were identified.[1]



Source: RMCO (1990, part 3)

Fig. 5. Trends in sulfur dioxide emissions and wet deposition of sulfate. Source: RMCO (1990, part 3).

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[1] Within that total, 54% of the lakes covered less than 1 hectare. Although such tiny lakes contain a relatively small proportion of the total supply of surface fresh water, they provide essential habitat for waterfowl and aquatic organisms (McNicol et al, 1987). Any influence that may disturb the balance of these vital ecosystems must be viewed with concern.

The task of gathering and evaluating data on all these lakes, ponds, wetlands, streams, and rivers is immense: at present, chemical analyses are available for only about 1% of the total. Even though some of the data were collected as early as the 1950s, systematic surveys have been conducted only during the last decade. Fortunately, this limited sampling base offers a reasonably good representation of the chemistry of the entire water resource, although there is a possibility that acidic and highly sensitive waters may be underrepresented.

Most of the unpolluted waters in eastern Canada are naturally very "soft" (low in dissolved minerals such as bicarbonate and therefore sensitive to acidic deposition) (LRTAP Working Group 1989) due to the bedrock and soil characteristics of the Canadian Shield. Such waters, unless otherwise polluted, will have a near-neutral acidity, ranging between pH 6 and somewhat greater than pH 7, and will contain only trace amounts of sulphate or nitrate (RMCC 1990, part 4).

When pollutants containing sulphuric and nitric acids are introduced into soft waters, the acids are first neutralized or buffeted by the bicarbonate and, to some extent, by the release of other elements, including aluminum. The evidence of such early acidification is most easily detected by the loss of bicarbonate and the appearance of sulphate in the water. At this stage, any nitrate that is deposited is usually assimilated as a nutrient by plants. It contributes directly to acidification of the water only when vegetation and other aquatic organisms cannot assimilate all that is deposited. When all the bicarbonate in the water body has been exhausted, the waters become significantly acidic, with a pH of 5.0 or lower. Researchers can measure the degree to which acidification has taken place in a lake by determining the relative amounts of bicarbonate and sulphate in samples of its water.

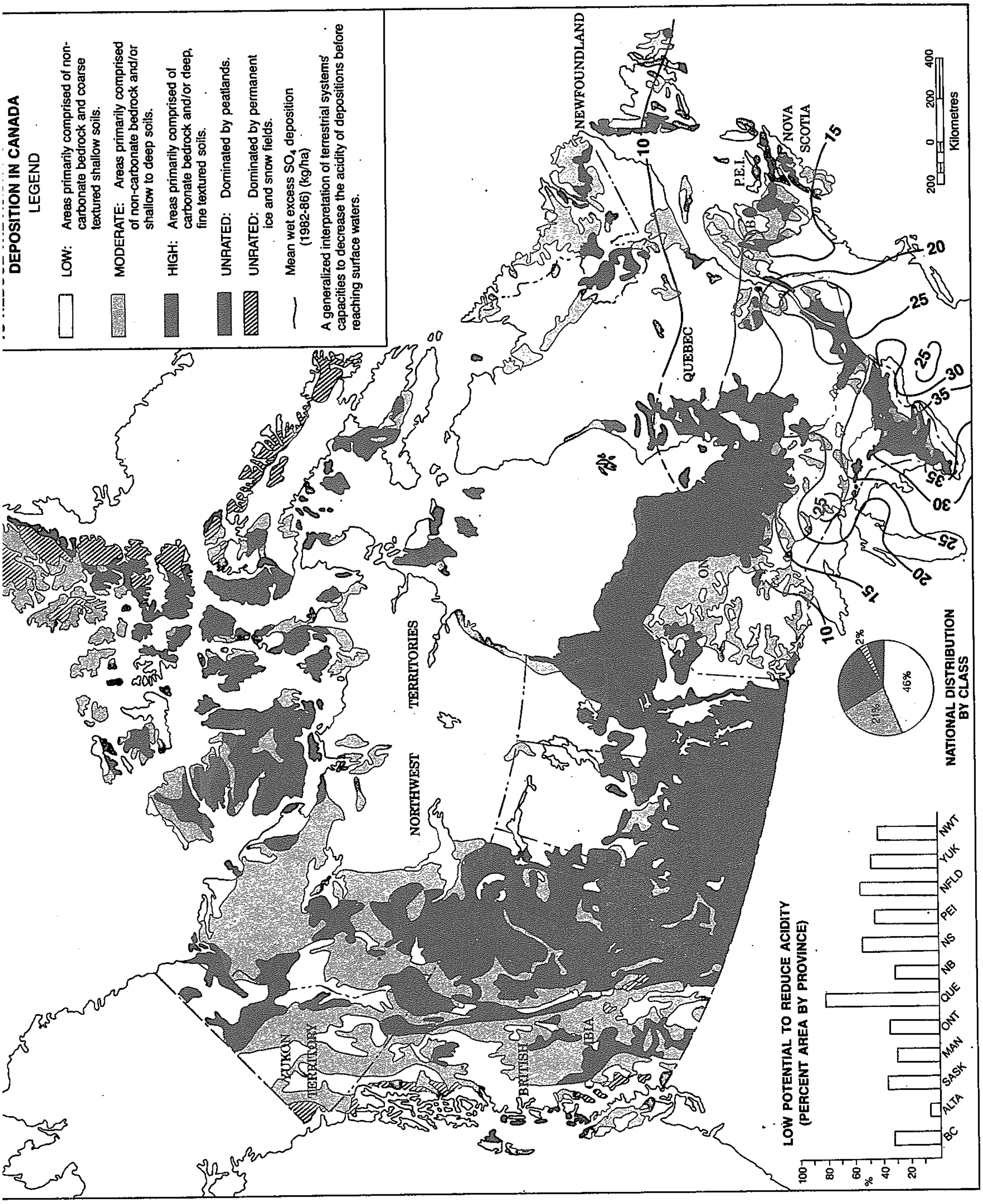
To determine how widespread the acidification of waters in southeastern Canada might be, more than 8,500 lakes have been surveyed and analyzed for their chemical content (RMCC 1990, part 4). Figure 8 summarizes the geographical distribution of waters according to the relative amounts of bicarbonate and sulphate. In areas where the ratio of bicarbonate to sulphate is less than one part bicarbonate to one part sulphate (shown on the figure as 1.0), the waters are experiencing serious acidification.

If the ratio has fallen to 1:5 (expressed as 0.2) or lower, it would be expected that many acidic water bodies with a pH below 5 would be found. As the map indicates, large portions of Ontario, Quebec, and the Atlantic provinces fall into these classes.

In addition to the long-term process of acidification, short-term events can have severe consequences for small bodies of water. In much of Canada, a large proportion of the total annual precipitation is deposited as snowfall, or in severe rainstorms. Sudden spring snowmelts and heavy storm runoffs have the potential to introduce large quantities of acidic pollutants into the surface water system in a very short time, introducing massive pulses of increased acidity to local streams and lakes. On occasion, these temporary pulses or "acid shocks" have killed large numbers of fish (Marmorek et al. 1987) before the sudden input of acidity could be buffeted. Because acidity in this form does not have time to be assimilated gradually into the environment, it is of particular concern, even in areas where long-term acidification has not yet reached levels that would normally be considered serious.

Changes in the flora and fauna of aquatic ecosystems are often the first and most immediate indicators of acidification in the lakes of eastern Canada. The interactions between living organisms and the chemistry of their water habitats are extremely complex. If a species or group of species increases or declines in number in response to acidification, then the ecosystem of the entire water body is likely to be affected. By causing direct change in a single component of the food web of an ecosystem, acidification can indirectly modify predator-prey relationships throughout the entire system. These indirect effects make accurate assessment of biological damage difficult, as it is necessary to understand which effects are caused directly by acidic pollution to draw dependable conclusions. By the time that a major biological response, such as the loss of a given fish stock, has become evident, serious damage may already have occurred in the aquatic ecosystem.

Knowledge relating biological responses to habitat acidification has been obtained from small-scale experiments in laboratories, from whole ecosystem experiments in which entire lakes are artificially acidified, and from extensive field surveys and monitoring (for some recent examples, see Figure 9). By combining these sources of information, quite a precise understanding of the effects of acidification on aquatic organisms has been obtained (RMCC 1990, part 4).



Source: RMCC (1990, part 4)

Fig. 6. The potential of atmospheric deposition in Canada.

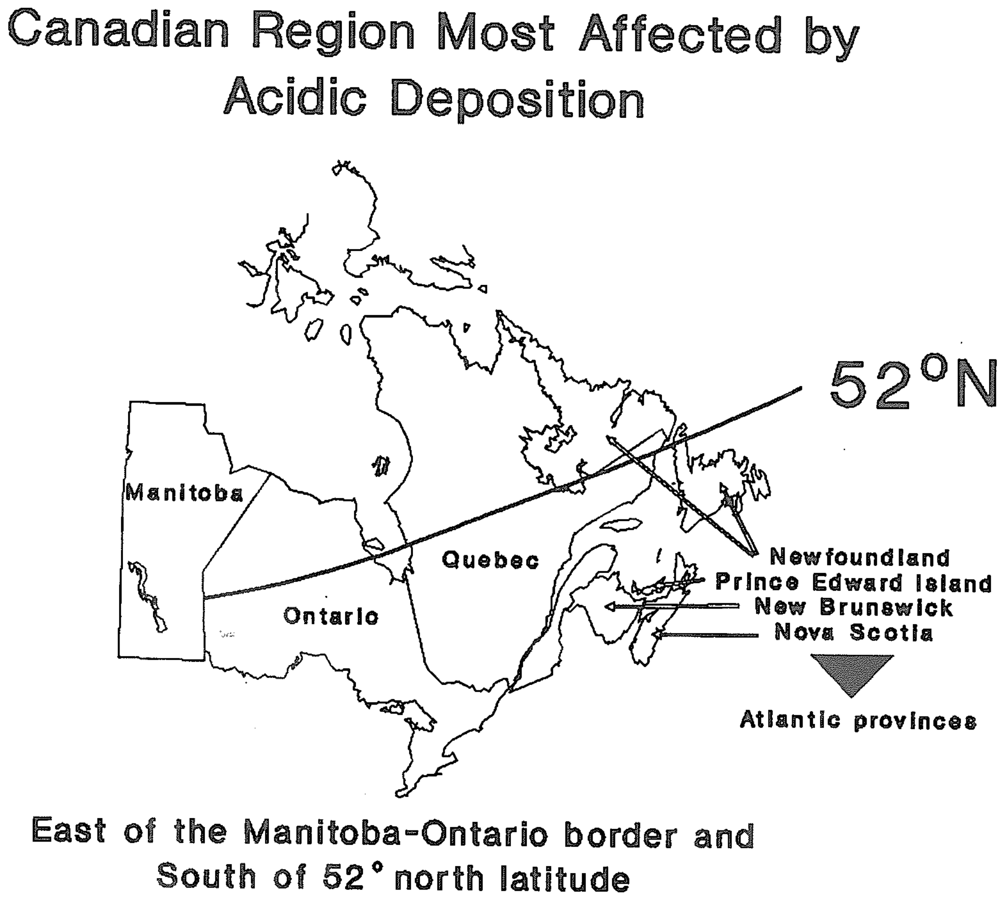
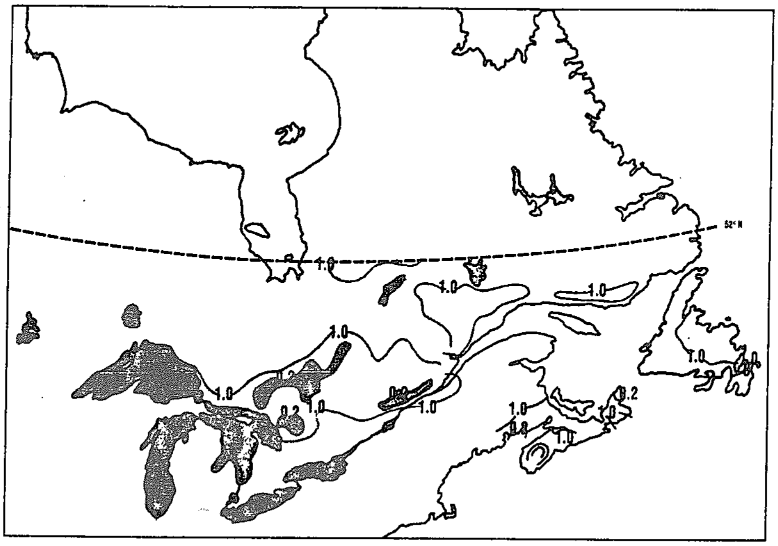


Fig. 7. The region of Canada that is most affected by acidic pollution.

At first, the effects may be almost imperceptible, but as acidity increases, more and more species of plants and animals decline or disappear (see Figure 10). Crustaceans, insects, and some algal and zooplankton species begin to disappear as the pH approaches 6.0, but most fish are not, as yet, affected directly. As acidity increases from pH 6.0 to pH 5.0, major changes in the makeup of the plankton community occur, and progressive losses of fish populations are likely, with the more highly valued species being generally the least tolerant of acidity. Fish declines often begin with reproductive failure, leaving a diminishing stock of aging individuals; when these fish die, their disappearance gives the impression of a sudden disaster, although the sequence of events leading to it may in fact have begun long before. At this stage of pH decline, less desirable species of mosses

Acidification of Waters
in eastern Canada



Numbers represent the ratio of bicarbonate to sulphate. Where the value is less than 1.0 (ratio 1:1), the waters are experiencing serious acidification.

Source: Jeffries (1991)

Fig. 8. Acidification of waters in eastern Canda. Source: Jeffries (1991).

and plankton may begin to invade. When the pH falls below 5.0, the water is largely devoid of fish, the bottom is covered with undecayed material, and the nearshore areas may be dominated by mosses. The lake, once rich in species, has gradually become an impoverished and unhealthy ecosystem.

Although most amphibians, such as frogs and salamanders, spend the greater part of their life cycle on land, they depend heavily on temporary ponds for breeding. These small, ephemeral water bodies are highly vulnerable to the "acid shock" events associated with storms and snowmelt. In several studies, reproduction of amphibians has been shown to be seriously restricted when the acidity of their breeding habitat increases to a pH value of less than 5.0 (RMCC 1990, part 4).

To date, water birds have not been shown to be directly affected by acidification. However, if acidification of their habitat should diminish the supply of fish, invertebrates, or plants on which they feed or induce elevated levels of toxic metals in the food supply, they may suffer the consequences. Invertebrates that normally supply calcium to egg-laying females and to their growing chicks are among the first species to disappear when lakes acidify. As these food sources are reduced or eliminated, the quality of habitat declines and the reproductive success of the birds is affected. Field studies have demonstrated that the Common Loon is able to raise fewer chicks, or none at all, on acidic lakes where fish populations have been reduced (Alvo et al. 1988; Wayland and McNicol 1990). On the other hand, there are some isolated cases in which food supplies for birds increase when competing species are removed. The Common Goldeneye, a species of duck that nests by lakes and rivers in forested terrain, can better exploit insects as food when competition from fish is eliminated. Such variations make the collective influences of acidification on bird populations difficult to quantify. Generally, however, acidification remains a continuing threat to species of waterfowl that rely on a healthy aquatic ecosystem for breeding and for rearing young, in thousands of lakes across southeastern Canada (RMCC 1990, part 4).

8.5 North American Controls on Acidic Pollutants

Canadian controls on acidic pollutants are based on protecting aquatic resources. For example, Canada's implementation of an emission control strategy required that a target level of pollution be specified as the objective of the plan. This level, or "target loading," was based on a realistic assessment of technical feasibility and economic and political costs, as well as environmental damages. In contrast, a "critical loading" has been defined as "highest load that will not cause chemical changes leading to long-term harmful effects leading to long-term harmful effects on the most sensitive ecological systems" (Nilsson 1986). A "target loading" policy objective will, from practical necessity, often be less stringent than the "critical loading." Some possibility of environmental damage will often be allowed. The Canadian Council of Resource and Environment Ministers (1983) established 20 kg/ha/yr as the target loading for the Canadian sulphur dioxide control strategy based on the level recommended to protect moderately sensitive surface waters (United States-Canada 1983).

Biological Response to Acidic Pollutants

Watt et al 1983	Decline in angling catch for Atlantic salmon associated with acidification of Nova Scotia rivers
Beggs et al 1985	Fish loss in regions affected by smelters at Sudbury and Wawa
Kelso et al 1986	Species diversity and richness reduced in low pH surface waters
Matuszek and Beggs 1988	Lower biotic diversity in Ontario lakes with pH < 6.0
ELA 1987	Food web disruptions can have significant and, in some cases, devastating effect on higher trophic level predator species
Harvey and Lee 1982	Observed fish kills in Plastic Lake in southcentral Ontario as a result of springmelt chemical episodes
Harvey and Whelpdale 1986	Spring runoff at a trout hatchery in southcentral Ontario reduced pH to 4.0 and caused fish mortality within 28 hours

Source: Jeffries (1991)

Fig. 9. Biological response to acidic pollutants. Source: Jeffries (1991).

Once this objective was established, existing knowledge of atmospheric transport processes was applied to estimate the amount of emission reduction that would be required. The levels of acidic sulphate that were deposited in 1980 (as high as 40 kg/ha at some sites [Figure 4] were accepted as the reference point for determining

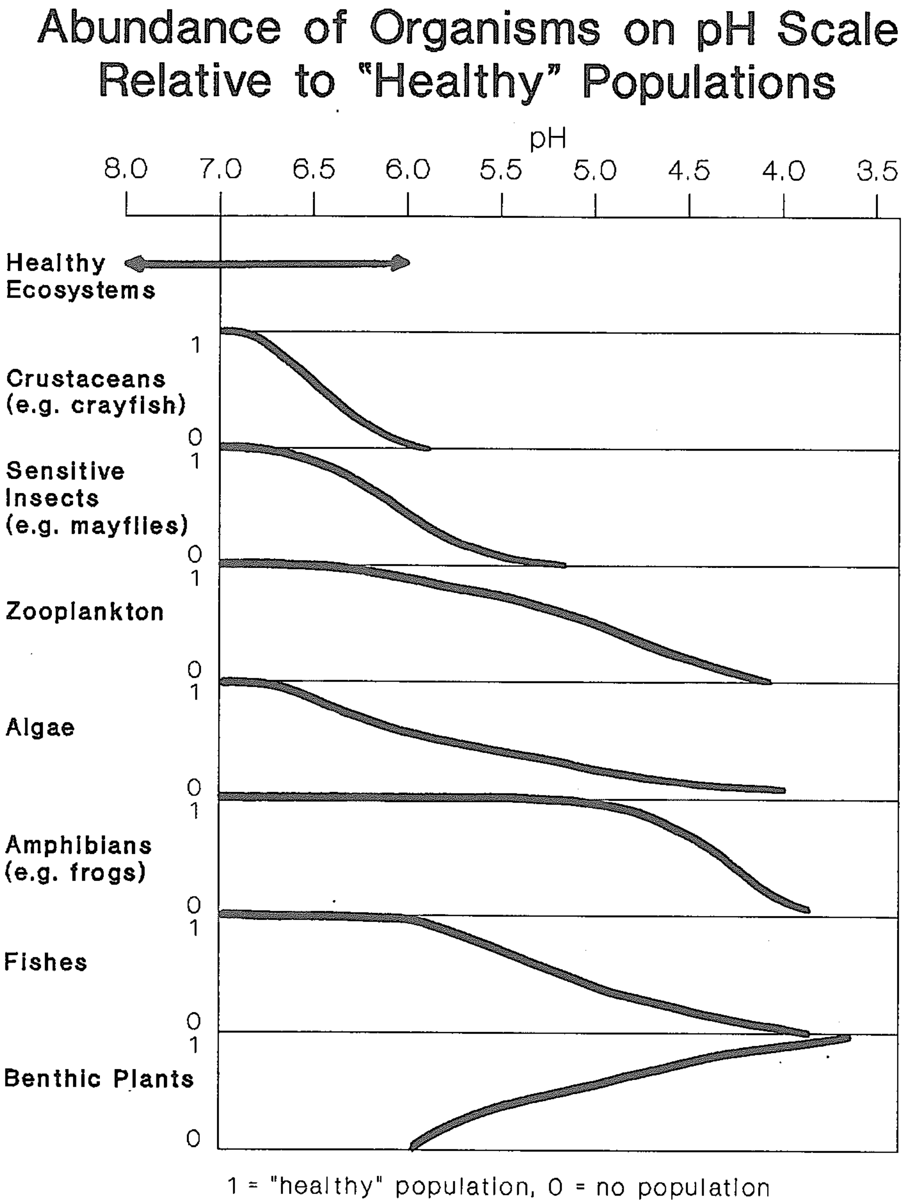


Fig. 10. Abondance of organisms on pH scale, relative to "healthy" populations.

control measures. Hence, the emission control strategy proposed that a 50% reduction in sulphur dioxide emissions would be needed to reach the desired target loading. Because roughly half the sulphate deposition recorded in 1980 was believed to originate from emissions in the United States, achieving a cooperative agreement with the United States would be an integral part of the overall control strategy. A reduction in the Canadian emissions alone could not achieve the deposition objective.

Federal/provincial negotiations were undertaken through the Canadian Council of Resource and Environment Ministers (CCREM). In February 1985, agreement was reached on the allocation of emission-reduction targets to each of the seven provinces from Manitoba eastward (Canadian Council of Resource and Environment Ministers 1985). Figure 3 depicts the progress and plans to reduce total emissions of sulphate in eastern Canada from a legislated limit of 4,500 kt in 1980 to 2,300 kt by 1994. The figure also shows the proportion of emission reduction assigned too smelters, fossil-fuel-powered electrical generating stations, and other sources. It should be noted that the actual emissions in eastern Canada in 1980 were only about 3,800 kt, as a result of early control efforts and existing market factors.

In the United States, amendments to the Clean Air Act, adopted in November 1990, form the legislative basis for control of sulphur and nitrogen oxide emissions. During pHase I, to be completed by 1995, emission limits for specific electric power generation stations will result in a total reduction of 5 million tons (4.5 million tonnes) in the annual emission of sulphur dioxide. During pHase II, to be completed by 2000, an additional 5 million ton reduction in the annual sulphur dioxide emissions will be assigned. Allowable limits on the emission of nitrogen oxides are to be established (U.S. Clean Air Act Amendments 1990).

In March 1991, *The Agreement between the Government of Canada and the Government of the United States of America on Air Quality*, commonly known as the Air Quality Accord, was signed to formalize each country's commitment to controlling acidic pollutants.

When these reductions in emissions are achieved in the United States and Canada, models of known transport-deposition patterns indicate that sulphate deposition will be below the 20 kg/ha/yr objective over all of eastern Canada (Environment Canada 1990). Although this reduction will substantially reduce the harmful effects of acidic precipitation, results of a recent study (Long-Range Transport of Air Pollutants Program 1990) indicate that various components of ecosystems, especially sensitive aquatic organisms, will still be at some risk (RMCC 1990, part 4).

Information in Figure 3 illustrates that the emission of sulphur in eastern Canada has declined over the past decade. The decline has made it possible to verify the dose-response relationship on which the control strategies have been based. A decline in sulphate deposition in Nova Scotia apparently resulted in reduced acidity in 11 rivers between 1971-73 and 1981-82 (Thompson 1986). In the Sudbury area, where emissions declined by over 50% between 1974-76 and 1981-83, a resurvey of 209 lakes shows that most of them became less acidic (Keller and Pitblado 1986). Surveys of 54 lakes in the Algoma region of Ontario showed a rapid response to a decline in sulphate deposition. Two lakes that in 1979 has a pH below 5.5 and were without fish have recovered sufficiently that their populations have been reestablished (Kelso and Jeffries 1988). Evidence is accumulating to support the benefits that were projected as a consequence of emission controls. This, in turn, provides increased confidence in the projections.

Models of atmospheric transport and deposition have been used to estimate the levels of acidic sulphate deposition that would be expected over Canada and the United States as a result of sulphur emission control. These levels of deposition have subsequently been used in models of aquatic systems to project the expected degree of acidification of lakes and the resulting impoverishment of fish species (i.e., the percentage remaining of the number of species present before acidification). Results show that emission controls provide a much greater benefit to the Ontario-Quebec area than to the highly sensitive lakes of the Atlantic provinces. Even with the U.S. controls in place, the modelled results indicate that some sensitive regions will still be expected to lose more than 10% of species in more than 30% of their surface waters. For the whole of eastern Canada, the area suffering damage would be reduced from about 100,000 lakes (13%) to about 39,000 lakes (5%) as a result of reductions committed to in the Canada-U.S. Air Quality Accord.

8.6 Summary

During the 1980s, the definitive symbol of the environmental crisis became the image of the biological death of lakes in remote wilderness as a result of "acid rain".

Acidic pollutants emitted from sources in the industrial heartland of the midwestern United States and central Canada regularly fall on the more rural and comparatively pristine areas of the northeastern United States and southeastern Canada.

Ontario, Quebec and the Atlantic provinces are Canadian regions that receive high levels of wet sulphate, and are areas of sensitive rock and soils least able to neutralize acidic pollutants.

Most of the unpolluted waters in eastern Canada are naturally low in dissolved minerals such as bicarbonate and therefore sensitive to acidic deposition. Large portions of Ontario, Quebec and the Atlantic provinces have a ratio of 1:5 bicarbonate to sulphate, where it would be expected that many acidic bodies with a pH below 5 would be found. Acid pulses or "shocks", as a result of spring snowmelts or heavy storm runoffs have killed large numbers of fish on occasion in some surface waters in Canada.

Changes in flora and fauna of aquatic ecosystems are often the first and most immediate indicators of acidification in the lakes of eastern Canada. Crustaceans, insects and some algal and zooplankton species disappear at pH 6.0; losses of fish populations begin as acidity increases from pH 6.0 to pH 5.0; amphibian reproduction is restricted at pH values less than 5.0; and water bird populations are indirectly affected by acidification.

Canadian controls of acidic pollutants are based on protecting aquatic resources. The Canada-U.S. Air Quality Accord formalizes each country's commitment to controlling acidic pollutants. Studies have shown that recent declines in sulphate deposition have resulted in a reduced acidity of lakes in Ontario as well as observed recovery of fish populations.

With controls in place, the modelled results indicate that sensitive regions of Canada would still be expected to lose more than 10% of species in more than 30% of their surface waters. A monitoring program has been established to regularly report on deposition and lake recovery. Control programs may be modified in light of these observations and the result of further research on forests and human health.

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APPENDIX
Acids, Bases and pH

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

$$HA \rightarrow H^+ + A^- \qquad (A1)$$

we have

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (A2)$$

where K_a = 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 K_a for a weak acid, the general expression (A2), may be used in a logarithmic form:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = pK_a + \log[A^-] - \log[HA] \qquad (A3)$$

multiplying both sides of the equation with -1 and using the symbol p for "-log" and pH for "-log H+".

It is often convenient to plot concentrations of HA and A- versus pH in a logarithmic diagram. If C denotes the total concentrations $C=[HA]+[A^-]$, we have at low pH:

$$[HA] \approx C$$

$$\log[A^-] = pH - pK_a + \log C \qquad (A4)$$

This means that $\log[A^-]$ increases linearly with increasing pH, the slope being +1. The line goes through (log C, pK_a) as $pH=pK_a$ gives $\log[A^-] = \log C$, see equation (A4).

Correspondingly, at high pH, $[A^-] = C$ and

$$\log [HA] = pK_a - pH + \log C \qquad (A5)$$

which implies that log[HA] decreases with increasing pH, the slope being -1. This line also goes through (logC, pK_a).

At $pH = pK_a$, $[A^-] = [HA] = C/2$ or $\log [A^-] = \log [HA] = \log C - 0.3$

Fig. A1 and Fig. A2 show the result of these considerations for a single acid-base system.

Note that for H_2A the slope will be -2 at $pH>pK_2$, corresponding to the dissociation of $2H^+$:

$H_2A \rightarrow 2H^+ + A^{2-}$ and for A^{2-} the slope will be +2 at $pH<pK$. This is demonstrated in Fig. 5.12.

ß, the buffer capacity, is defined as $\beta = dC / dpH$.

It can now be shown that

$$\log \left(\frac{\beta}{2.3}\right) = \log \left([H_3O^+] + [OH^-] + \sum \frac{[A^-]\,[HA]}{C} \right) \qquad (A6)$$

At log pH $[HA] = C$, and only $[H_3O^+]$ plays a role.

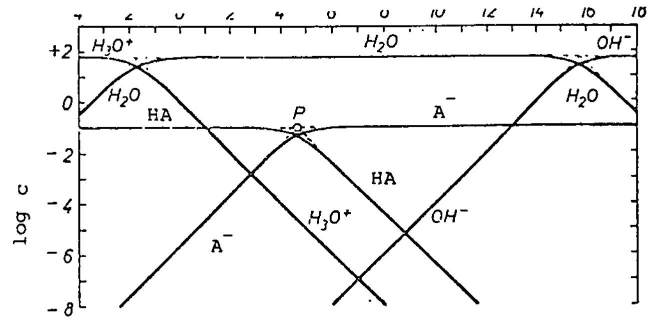

Fig. A1 H3O+, OH- and water + HA/A-. pKa = 4.64 and C = 0.1 M.

At higher pH, $\dfrac{[A^-][HA]}{C}$ = $[A^-]$ also contributes to $\dfrac{\beta}{2.3}$

where $[H_3O^+] = [A^-]$, $\log\left(\dfrac{\beta}{2.3}\right) = \log\left(2\,[H_3O^+]\right) = -pH + 0.3 = \log\left(2\,[A^-]\right)$.

At still higher pH, but with values of $pH<pK_a$, $\log [A^-]$ dominates.

At $pH = pK_a$ $\log\dfrac{\beta}{2.3} = \log\dfrac{C/2 * C/2}{C} = \log\dfrac{C}{4} = \log C - 0.6$

At $pH>pK_a$, $[A^-] = C$ and $\log [HA]$ contributes the most to $\dfrac{\beta}{2.3}$

At very high pH, $\log [OH^-]$ will dominate. These considerations are used in the construction of Fig. A2.

Fig. A3 is a double logarithmic diagram for seawater. The proteolytic species mentioned above are represented in their appropriate concentrations. The important species are hydrogen and hydroxide ions, boric acid (HB) and carbonate ions (C^{2-}). The arrow in the diagram indicates the pH value of seawater - about 8.1.

Based on such a diagram it is possible to set up another diagram, representing the buffering capacity as a function of pH, see Fig. A4. For those who are interested in the relationship between the two diagrams, see Hägg (1979).

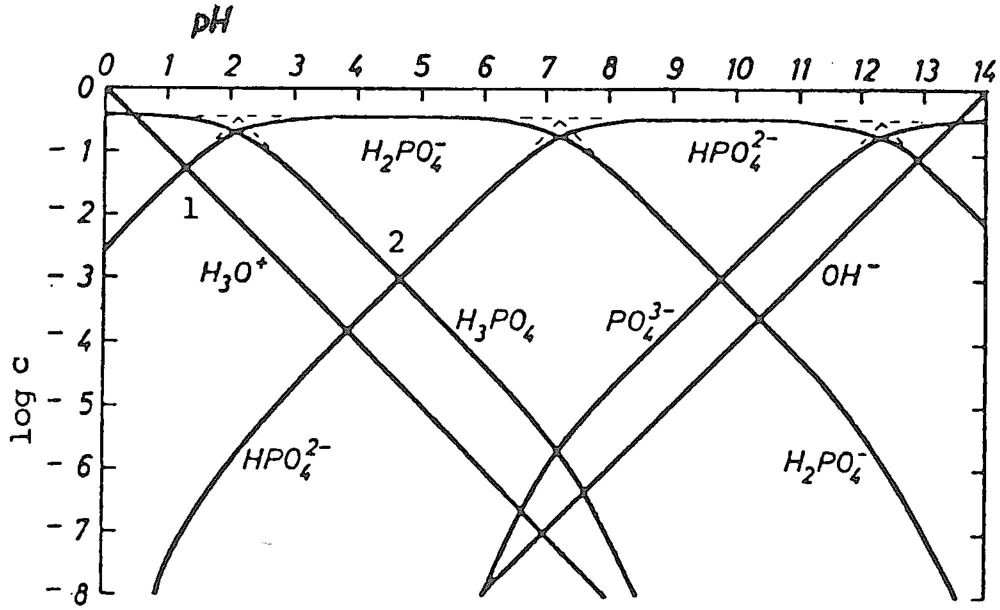

Fig. A2 pH-log c diagram for phosphoric acid.

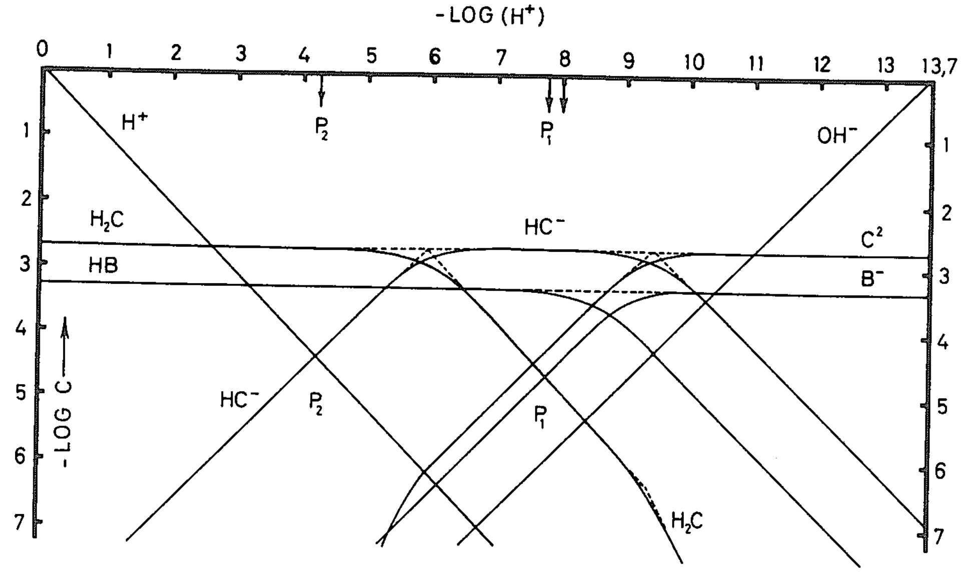

Fig. A3: pH-diagram. H2C = H2CO3, HC- = HCO3-, C2 = CO32-, B- = borate. pH of the sea is indicated by an arrow.

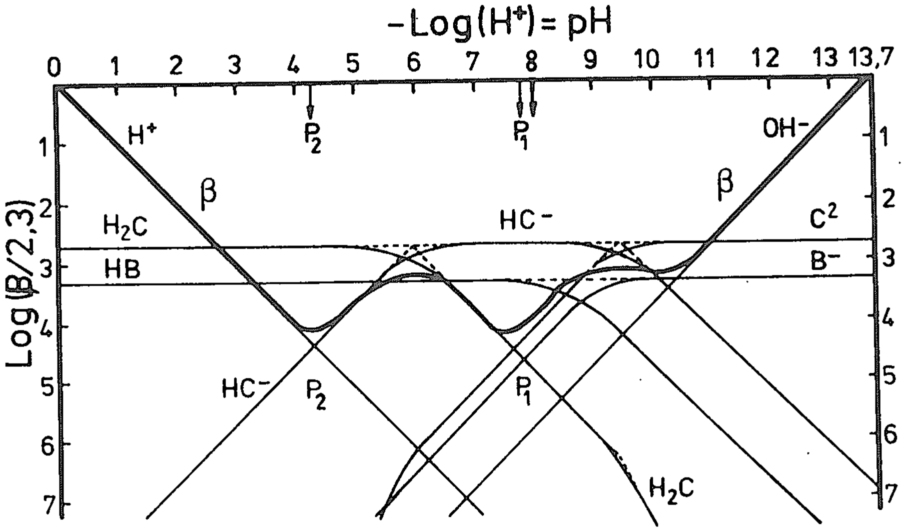

Fig. A4 Buffering capacity of the sea as a function of pH (β).

APPENDIX 2

Global Acidic Atmospheric Deposition

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Acidification of surface ecosystems results from the combination of sensitive soils and lakes and acidic atmospheric deposition. The main chemical constituent of acid deposition are oxides of sulfur and nitrogen, with chloride and some organic acids contributing to a lesser degree.

Figure A5 shows schematically regions of the world where soils are sensitive to acid deposition and regions where high emissions of acidifying pollutants occur. Locations that combine sensitive soils and high emissions - parts of eastern North America, northern and central Europe, and southern China - represent today's problem areas. Potential problem areas, identified by soil sensitivity and expected future emission rates are also shown in Fig. A5.

Both wet and dry atmospheric deposition contribute to acidification. Wet deposition is measured in many parts of the world, and extensive data are available in North America, Europe, and parts of Asia. However, yet, a reliable global wet deposition data base does not exist. Dry deposition estimates, derived from ambient concentration measurements, are even more limited.

An alternative approach to estimate global wet deposition is to use large-scale chemical transport models. Figure A6 shows calculated annual wet deposition of non-sea-salt sulfur (Langner and Rohde, 1991). Since sulfur is the main contributor to precipitation acidity, the areas of high sulfur deposition are identical with the problem areas that appear in Fig. A5.

Agreement between model predictions and observations is generally rather good. For example, the predicted wet deposition rates over eastern North America and Europe up to > 1 g S / m^2 / y compare favorably with the observed maxima of about 1 and 2 g S / m^2 / y in North America (Vet et al., 1992) and Europe (Hanssen et al., 1990) respectively. In remote areas, modelled sulfur deposition is in the range of 50 - 250 mg S / m^2 / y, while observations are in the range of 30 - 400 mg S / m^2 / y (Galloway, 1985).

An intensive effort is now underway through the World Meteorological Organization and the United Nations Environment Program to augment global monitoring of precipitation composition and deposition within the Global Atmosphere Watch, and to prepare a comprehensive global assessment of acid deposition.

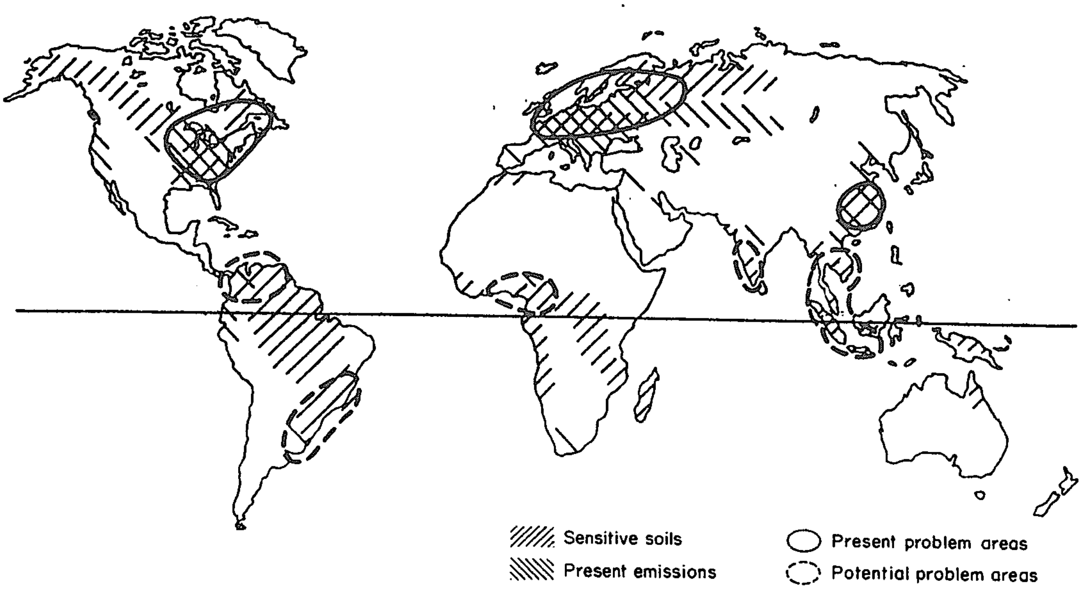
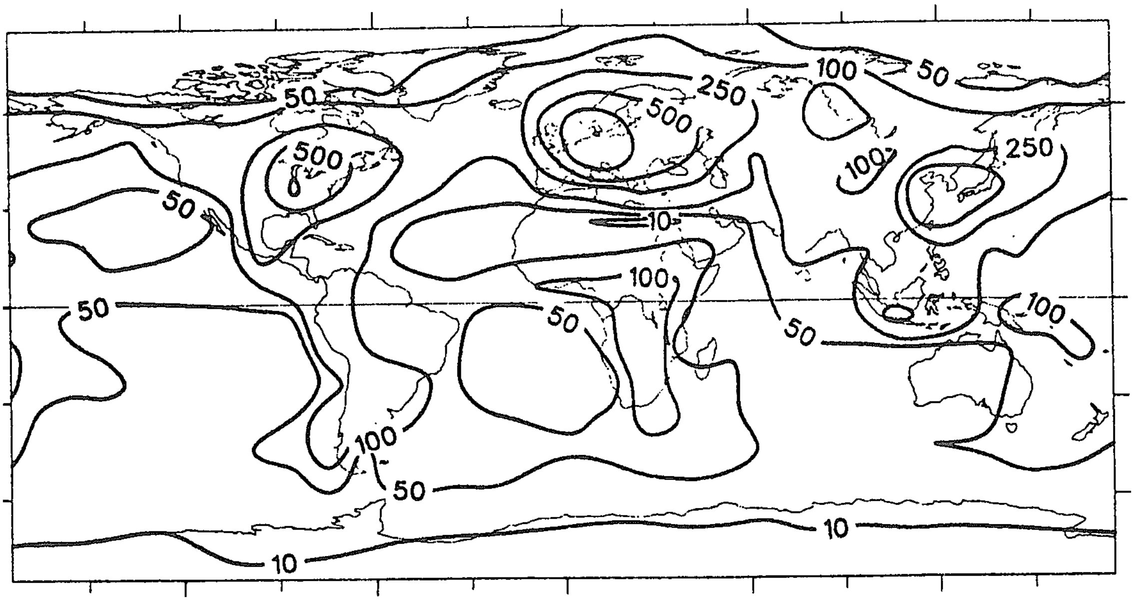


Fig. A5 Schematic map showing regions that currently have acidification problems, and regions where, based on soil sensitivity, expected further emission and population density, acidification might become severe in the future. Reproduced from Rohde and Herrera (editors), 1988.



Isolines are: 10, 50, 100, 250, 500, 1000

Fig. A6 Calculated annual wet deposition of non-sea-salt. Reproduced from Langner and Rohde, 1991.

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Table 2.2 Characteristics of the most important greenhouse gases (Rounded figures). The global warming potentials (GWP) and relative contributions are calculated for a time horizon of 100 years. Emissions are only anthropogenic. For the hydrocarbons (NMHC) and chlorofluorocarbons (FC) total and average values are given.

Compound	Lifetime years	Global emission mio ton/year	GWP rel. CO_2	Contribution %
CO_2	120	26.000	1	61
CH_4	10	300	21	15
N_2O	150	6	290	4
CO		200	3	1
NO_x		66	40	6
NMHC		20	11	1
CFC	100	1	5000	12

Table 2.3 The must important characteristics of ozone depleting compounds (Rounded figures).

Compound	Lifetime years	Global emission mio ton/year	GWP rel. CO_2	Contribution %
$CFCl_3$ (CFC 11)	140	340	1	30
CF_2Cl (CFC 12)	120	440	1	40
CCl_4	150	100	1	10
$C_2F_3Cl_3$ (CFC 113)	90	160	0.8	12
CHF_2Cl (CFC 22)	90	200	0.07	1
$C_2H_3Cl_3$	130	550	0.1	5
$CBrF_3$ (Halon 1301)	150	2	10	2

Table 2.1 Emission factors for use of fossil and a few other fuels in Denmark. Unit kg/GJ.

Fuel % sulphur	Application	SO_2	NO_x	CO_2	N_2O	CH_4	NMVOC
Coal							
1,0	Power plants	0,714	0,440	95,0	0,003	0,0003	
0,9	District heating	0,584	0,200	95,0	0,003	0,0002	
0,9	Process (industry)	0,584	0,200	95,0	0,003	0,0003	
Fuel oil							
1,0	Power plants	0,495	0,280	78,0	0,003	0,0001	
1,0	District heating	0,495	0,150	78,0	0,003	0,0001	
1,0	Process (industry)	0,495	0,150	78,0	0,003	0,0001	
1,0	Ships	0,495	1,733	78,0	0,051	0,0083	0,1987
Diesel oil							
0,2	Cars <3,5 t	0,094	0,303	74,0	0,009	0,0050	0,1190
0,2	Cars >3,5 t	0,094	1,509	74,0	0,051	0,0072	0,1738
0,2	Ships	0,094	1,733	74,0	0,051	0,0083	0,1987
Gas oil							
0,2	District heating	0,094	0,100	74,0	0,003	0,0001	
0,2	Domestic heating	0,094	0,050	74,0	0,003	0,0030	
0,2	Process (industry)	0,094	0,100	74,0	0,003	0,0001	
Petrol							
0,05	Cars	0,022	0,723	73,0	0,022	0,0974	1,1676
Natural gas							
~0	Power plants	~0	0,240	56,9	0,002	0,0003	
~0	Gas turbine	~0	0,200	56,9	0,0002	0,0003	
~0	Gas engine	~0	0,200	56,9	0,0002	0,0003	
~0	Process (industry)	~0	0,100	56,9	0,002	0,0003	
~0	District heating	~0	0,150	56,9	0,002	0,0003	
~0	Domestic heating	~0	0,050	56,9	0,002	0,0010	
Waste							
0,3	District heating	0,675	0,150	117,0	0,003	0,0003	
Straw							
0,1	District heating	0,130	0,130	102,0	0,003	0,0002	
0,1	Domestic heating	0,130	0,050	102,0	0,003	0,1500	
Biogas							
~0		~0	0,05-0,15	56,9	0,002	0,0003	