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The dynamics of Lake, Bog & Bay–Consequences of exposure to man related to final storage of spent nuclear fuel.

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Studsvik Energiteknik AB, December 1984

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

A list of other reports published in this series during 1984 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28) and 1983 TR 83-77) is available through SKB.

THE DYNAMICS OF LAKE, BOG & BAY - CONSEQUENCES
OF EXPOSURE TO MAN RELATED TO FINAL STORAGE OF
SPENT NUCLEAR FUEL

A b s t r a c t

The natural ageing of the environment, much shorter than a possible continuous release from a repository, results in uncertainties as regards to consequences of exposure to man related to final storage of spent fuel.

The Phase I project summarizes the identification of such factors and parameters of predominant importance for an assessment of possible radiological consequences in a normally revolving biosphere.

Three major areas are described: geomorphology and residence time such as phenomena associated with the formation of lakes in Sweden formed by the latest inland ice, lake development in terms of uptake of different elements and radionuclides as a function of the chemical composition of the water in a recipient and some aspects of sedimentation in lakes and coastal waters.

The chemical environment is also studied in the evolution of a lake or a Baltic bay into farming land or peat land. The most important parameters to the behaviour of trace metal ions seem to be pH, Eh, ionic strength and content of complex formers.

Finally, the human impact during the evolution of a lake or a bay is discussed.

The study also includes recommendation for a reference field test area and for laboratory studies of the chemical properties of radionuclides in sediments in a Phase 2 project.

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THE DYNAMICS OF LAKE, BOG & BAY - CONSEQUENCES
OF EXPOSURE TO MAN RELATED TO FINAL STORAGE OF
SPENT NUCLEAR FUEL

BACKGROUND

With groundwater as a pathway radioactive material may reach the biosphere and man. The characteristics of the recipient of the biosphere is therefore of major importance for the dispersion of radionuclides.

The natural ageing of the environment - much shorter than a possible continuous release from a repository - results in uncertainties as regards to the assessment of possible radiological consequences.

The purpose of this initial study aims to define parameters of predominant importance concerning the transfer of radionuclides from groundwater to man and quantitatively determine the changes.

Phase 1 of the project also includes recommendation for a reference field test area of Sibbo- and Trobbofjärden and laboratory studies of the characteristics of the chemical properties of radionuclides in sediment.

*

To launch a project of this kind initiated some brain-storming activities. Approaches were many in order to include all scopes of ideas but after having structured the major processes affecting the evolution of lakes and given priority parameters governing the various development stages the point of interest focused on three major areas of importance;

| | | |
|--------------------------------------|--|--|
| Geomorphology & Residence time | Lake Development - Flora & Fauna | Sedimentology: accumulation & resuspension |
|--------------------------------------|--|--|

These three areas are described in the following reports:

- (1) Lake and Coastal Zone Evolution during Postglacial Time (B Sundblad)
- (2) The Ageing of a Lake Changes in Plant and Animal Life. (P O Agnedal)
- (3) Aspects on Sedimentation in Lakes and Coastal Waters (S Evans)

The chemical environment is a continuous process during the development of lakes and coastal waters. The trace metal chemistry release into a lake, river or sea is therefore treated in a separate report:

- (4) Chemical Properties of Lake Sediments and Peat of Importance to Trace Metal Behaviour (K Andersson)

Finally, a fifth study describes some aspects on the evolution effects on man by fertilization and terrestrialization:

- (5) Human impact during the evolution of a lake or a bay (A-B Wilkens).

CONCLUSIONS OF REPORTS

Appendix 1. Lake and coastal zone evolution during postglacial time (Björn Sundblad)

Most of the recent lakes in Sweden are originally formed by the latest inland ice. However, the lakes are occasional phenomena. Many processes affect the evolution of the lake. Some of these are discussed in this report.

The lake evolution goes through several stages, where the importance of the different processes will change.

The water is the carrier system for suspended material, d_i solved substances, biomass etc. Because of that it is important to know the residence time during different stages of the lake evolution.

The sedimentation is also dependent on the water transport to and within the lake. The unknown relation between sedimentation rate and residence time must be solved, to be able to find the transfer coefficients between water and sediment, and their variations. The water transport also affects the horizontal and vertical distribution of the sedimentation.

Another important parameter is the stratification of the lake, mainly the thermal stratification.

A reduced vertical water exchange will for example affect the oxygen condition at the bottom.

At the coastal areas the transition from brackish water to fresh water is different from the pure lake systems for stratification, sedimentation etc. Because of that the transition period must be treated separately in the lake evolution. The Sibbofjärden-Trobbofjärden area are suitable to study these differences.

Appendix 2. The ageing of a lake - changes in plant and animal life (P O Agnedal)

The uptake of different elements and also of radioactive nuclides varies with the chemical composition of the water in a recipient. The uptake varies with different species of both plants and animals.

It is therefore important to have a good knowledge of conditions such as pH, redox-potential, nutrient contents, composition of flora and fauna in order to be able to calculate how much of an element will be accumulated by plants and animals and how much will be transported to the sediment after decomposition.

The uptake is also depending on the total production of organic material in the different trophic layers.

As has been reported the production can vary very much both during the year and in each trophic layer.

In an American lake the production of rooted vegetation was 50 kg dw/har per year and of phytoplankton 2560 kg dw/har. The fish catch varies from less than 5 kg/har up to 20 kg/har depending on the type of lake.

In order to be able to calculate the amount of an element bound in each trophic layer a knowledge of the production seems necessary.

It can therefore be deemed necessary to study the transport of some elements in the different lake types and also in the peat and from these studies try to draw conclusions of the behaviour of those radionuclides which might be of interest.

Comparably laboratory studies of the transport mechanisms should also be investigated step by step in laboratory experiments where the lake types are simulated.

Appendix 3. Aspects of sedimentation in lakes and coastal waters (S Evans)

Theoretical models of ecological processes in estuarine and lacustrine environments call for data suited to calculate sediment budgets in relation to space and time. Accurate long-term forecasts on sediment growth and the subsequent accumulation of elements in the deposits laid down require knowledge about production rates and sources of particulate matter, sedimentation rates, affinity of elements to solids, mobility of elements when deposited on the sediment bed etc. Efforts to model sediment dynamics must be based on parameters based on field measurements together with data extrapolated from laboratory experiments.

The sediments are subjected to various short-term perturbations such as seasonal variations in the sedimentation rate, resuspension by near bottom currents and bioturbation due to the micro- and macrobiological activity occurring within the deposits. Consequently, the sediments from a defined layer only provide information integrated over longer periods. The resolution in time is highly governed by the sedimentation rate which varies from about 50 g m^{-2} in oligotrophic waters to about $3\ 000 \text{ g m}^{-2}$ in eutrophic waters. Thus the measurement of the seasonal sedimentation rate is of crucial importance for the interpretation of the dynamics of the bottom boundary layer of a water body. Furthermore, the physical and biological factors disturbing the deposits laid down will to a large extent govern the chemical status of the sediment bed.

The interstitial water within the sediment layer serves as a carrier of elements between the sediments and the overlaying water. This will enable chemical species to migrate within the sediment as well as across the sediment-water interface. However, a limited number of physical sediment parameters such as water content, organic content, bulk density and grain size will generally be enough in order to make an accurate classification of the sediment. Most other physical sediment parameters like porosity, permeability and compaction may be defined in terms of these basic parameters.

Appendix 4. Chemical properties of lake sediments and peat of importance for trace metal behaviour (K Andersson)

In the evolution of a lake or a Baltic bay into farming land or peatland a wide range of

possible chemical conditions may be expected to occur within bottom sediments and in the peat.

There are some parameters in the interstitial water which are of large importance to the behaviour of trace metal ions. The most important seems to be pH, Eh, ionic strength and content of complex formers.

pH may vary from 3.5 to over 8. The low values are most likely to occur in peat and in acid soils, while pH values of 7 to 8 are the most common in sediments. Also in some types of peat pH up to 7 may occur. Since the possible sorption of cations usually is increasing with pH, especially for easily hydrolyzed ions, the systems with high pH may be expected to exhibit a lower mobility of trace cations.

The absolute value of the redox potential, Eh, is a quantity that is difficult (or impossible) to determine. A significant difference between oxic and anoxic conditions may although be observed. In sediments Eh changes may occur over the year, especially in the surface layer due to variations in the aeration and oxygen consumption of the overlaying lake water. Deep sediments and peats also tend to be depleted of oxygen. The behaviour of redox sensitive metals (e.g. Tc, U, Pu) may be determined by the redox conditions to a very large degree, while for others there is one predominant valence state and the redox conditions will only be of importance if they influence the properties of the solid or water chemistry.

The ionic strength is also varying over a wide range for the water types in question. The amount of dissolved ions may be from some mg/l

up to 16 000 mg/l. This means that the sorption may vary very much for uncomplexed cations depending on the type of water. Also the complexation is dependent of the ionic strength (stability constants decrease with increasing ionic strength).

In all the water types discussed, the content of potential complex formers may be quite high. Among these there are both inorganic species like phosphate, carbonate and sulphate and organic compounds (humic substances). The influence of complex formers may be due to several mechanisms. They form complexes with trace metals that may be both more and less soluble than the uncomplexed ion. The complexes may also be sorbed to a higher or lesser degree than the uncomplexed ion. There may also be a sorption of organic complexants on the mineral surfaces that inhibit sorption of metal ions. Complexation may occur with both macro and trace components and competition has thus also to be considered.

Complexation may occur with solid organic substances. This may in some cases be virtually irreversible.

The properties of the solid mineral phases present are also of large importance to the behaviour of trace metals. Metal ions may be sorbed on the surfaces, causing both reversible and irreversible incorporation into the solid phase. The interstitial water composition is also influenced by the solid phases. The interactions may however be slow, and equilibrium conditions cannot always be expected.

Some general conclusions on the behaviour of trace metals in peat may be drawn from

investigations of metal enrichments in nature. Observations have been made on the difference in the occurrence of uranium and lead in peat deposits. Also conclusions on the plant availability have been drawn from this type of investigations. The investigations show enrichments of uranium in and lead in the bottom layers of peat, while lead is enriched also on the surface.

Radium seems to be stronger bound to the organic solids than is uranium, and here the competition with calcium is important.

Appendix 5. Human impact during the evolution of a lake or a bay (A-B Wilkens)

The effects of human impact can as well accelerate as counteract the development of a lake or a bay, but most influences increase the ageing rate during the different stages, for instance:

- During the eutrophication: Fertilization of arable land in the catchment area may lead to nutrient losses with drainage and surface water, above all phosphorus and nitrogen, with increased eutrophication as consequence.
- Clearcutting of forests combined with fertilization, drainage and liming may give rapid release of nutrients to surrounding lakes.
- Ammonium containing fertilizers are under aerobic conditions enzymic oxidized to nitrate form leading to decreasing soil pH with increased solubility and mobility of cations, including heavy metals and radionuclides.
- Outlets of waste water from industries and households may accelerate the ageing rate of the recipient.

- Aquaculture may cause release of phosphorus and other pollutants in the lake water.
- Ditching of surrounding areas may lead to changes in the water balance in the recipient and in the water chemistry.
- In association with the terrestrialization: Drainage of a lake to get new agricultural soils leads to oxidation in the upper soil layers. Organic and inorganic sulphur may be oxidized to SO_4^{2-} and the soil will be acidified. The solubility and mobility of heavy metals and radionuclides will increase.
- More and more aerobic conditions in the upper layers of the soil leads to enzymic oxidation of nitrogen compounds to nitrate form and a lower pH as a consequence.

The release and transport of pollutants from sediment in organic soils may be influenced by for instance following factors:

- Oxidation processes and decomposition in organic soils due to drainage and cultivation.
- Uptake via roots of metal ions in connection to crop production and grazing.
- Release of pollutants in drainage water and transport to the recipient.
- Lowering of pH in soils due to acid rain may change the solubility and perhaps also the plant availability of metals.
- Use of peats and biomass in energy production may lead to dispersion of pollutants in the environment.

The effects mentioned above are examples of impacts that are common or may be expected today. Other human activities in the future may naturally lead to hitherto unknown effects.

PHASE 2

BACKGROUND

The first stage of this study aimed to describe the wide range of parameters, some of them with greater importance than others, governing the pathways of radionuclides from groundwater to man. The initial project could be summarized as the identification of factors and parameters of predominant importance for an assessment of possible radiological consequences in a normally revolving biosphere.

Furthermore, the study included recommendations for a reference field test area and for laboratory studies of the chemical properties of radionuclides in sediments.

PROJECT DESCRIPTION

In order to reach an more detailed understanding of the consequences of the potential release of radionuclides into the biosphere from an underground repository, the phase 2 of the study is suggested to focus on the quantification evolution of lakes and coastal waters and their sediment. The main purpose of the Phase 2 project is therefore to explain the transfer mechanism and to identify possible accumulation of radionuclides from groundwater to man during different periods of the development of a recipient area and quantitatively determine the changes.

The proposed area of investigation is the precipitation area of two outflows called Sibbo- and Trobbofjärden, approximately 20 kilometers east of Nyköping. The lake system in this area

represents typical lakes in the southern and middle region of the Swedish coastal and rural area.

The Trobbofjärden is a lake which was cut off from the sea some 30 years ago by human impact. By land uplift, the Sibbofjärden is today a fresh-brackish bay linked to the sea by a narrow passage. The transition of two separate systems from sea to lake can therefore be studied in a unique way related to time.

The proposed project is divided into three major categories:

1) field studies, including

- sampling of sediments along profiles from surrounding solid ground to deep lake sediments in order to cover lake sediments of different age and character,
- discharge measurements and water sampling of macro constituents and suspended material for estimation of material and water balance of the lake,
- determination of the annual growth of sediment and its yearly cycle by using sedimentation traps at different sites and depths,
- mapping of vegetation for the determination of biomass production.

2) chemical studies, comprising

- determination of the pore water composition in the sediments. Parameters of importance to the mobility of trace metals such as pH, Eh, pS^{2-} , ionic strength and contents of complex formers will be determined,
- characterization of the solid sediment phase. Measurement of organic content, cation exchange

capacity and in some cases surface area and mineralogy,

- trace metal distribution between pore water and solid to provide information on the mobility of naturally occurring trace metals in sediments. The data may be used in predicting the transport of radionuclides in sediments,
- the influence of organic complex formers on the mobility of trace metals. Fractionation according to molecular weight of trace metal complexes in the pore water gives information on the influence of organic complex formers on the mobility.

3) transport study of radionuclides in sediments

- in situ studies to verify the transport of actinides and fission products in sediment. Sediment cores are collected in the recipient. The nuclide is implanted at different depths in the core. Thereafter these are transferred back to the recipient. On subsequent occasions the cores are recollected and the distribution of the nuclide within the core is recorded. The migration is correlated to the physical and chemical sediment properties.

TIME SCHEDULE

The Phase 2 project is planned to start up in early 1985 and continue through to mid-86 according to the following preliminary schedule:

| | 1985 | 1986 | 1987 |
|---------------------------|-------|-------|------|
| Field studies: | | | |
| Water balance | ----- | | |
| Material bal | ----- | | |
| Mapping of vegetation | --- | --- | |
| Sedimentation sampling | _____ | _____ | |

Chemical studies:

Pore water
composition,
solid phase,
trace metal
distribution,
organic
formers

Sedimentation studies:

Core sampling ___ ___

Progress of work will be reported regularly and discussions held in order to evaluate on-going results. A report of Phase 2 is planned for June 1986.

In a Phase 3 the material will be used for the validation and/or development of biosphere models.

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Björn Sundblad

LAKE AND COASTAL ZONE EVOLUTION
DURING POSTGLACIAL TIME

ABSTRACT

The most important climatological and geomorphological processes governing the evolution of lakes, from a physical point of view, are discussed. The classification of the Swedish lakes based on the area of the lakes and the geomorphological regions is presented.

The coastal zone evolution, including land uplift and examples from some areas along the Swedish coast, is also presented. In one of these areas, Sibbofjärden close to Studsvik, a field survey has been carried out. The salinity, pH, temperature and depths have been measured.

Rough estimates of the time scale for lake evolution from present lake to dry land have been done.

Estimates of the present residence time for different hydrological regions and lake types are also included in the study.

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1 INTRODUCTION

The landscape is continuously changing. Large areas of the present landscape have formerly been at the bottoms of lakes and seas.

Because of the land uplift new land areas will be formed. Coastal bays can become lakes in the future.

A lake will be changed in many ways during its lifetime. There are many processes governing these changes, including geomorphological, climatological, biological and hydrological processes and human impact.

The above mentioned processes contribute to the terrestrialization of a lake, which in most cases is a natural process. The lake normally ages slowly by silting up, whereby the vegetation migrates out into the lake. This process is slow in the early stages, but it usually accelerates during the evolution.

Under natural conditions the ageing process takes thousands of years. However, nutrients from households, industries and farming, are transported to the lakes and the process is accelerated by the human impact. The nutrients can also be brought to the lake by cultivation, draining and clear-cutting within the catchment area.

Processes at the bottom and within the uppermost layer of the sediments are essential for the terrestrialization of a lake. Furthermore, the sediments are often the greatest reservoir of radionuclides which have been brought to the water recipient. Thus in the future the

sediments formed earlier can be brought into cultivation and the radionuclides can begin to circulate in the biosphere again.

2 PROCESSES GOVERNING LAKE EVOLUTION

2.1 Climatological Processes

From a climatological point of view it is mainly the air temperature and the precipitation that affect the level of a lake.

A humid cold climate means a high discharge into a lake and little evaporation. As a result of these conditions the lake level will be high. The opposite, a dry warm climate, leads to decreasing lake levels because of high evapo-transpiration and a low discharge.

There are examples of both these extremes of climatic type during the post-glacial period. About 9000 years BP, in the Ancylus era of the Baltic, the climate was warm and dry. During this dry period some lakes dried out completely. Others lost their outlet and because of the high evaporation they were enriched in salts and became brackish.

After the Ancylus era the Littorina Sea period began. The temperature was still high, about 2-3°C above the summer temperatures nowadays. However the climate became more humid and the discharge increased, so that the lake levels rose again.

These two periods are examples of variations over a long time span. However, the duration of the fluctuation can be much shorter, for example over decades.

2.2 Geomorphological Processes

Geomorphology is the science of forms of the earth, their origin and development.

A lake is usually formed in a fast way by tectonic movements in the earth crust, or as a result of the effect of inland ice on the landscape. On the other hand the ageing is a slow process. However, human impact can accelerate the conversion of open water to dry land.

The so called exogenous forces erode the earth's surface. The main exogenous processes are (Lundegårdh, 1964):

- mechanical and chemical weathering
- fluvial activity by running water
- glacial activity by ice
- eolian activity by the wind
- marine activity by the sea
- biogenous activity by man and the "organic world"

All these processes act in the same direction, i.e. to level the landscape. The water is the transport system and this means that large quantities of the eroded material will be transported to the lakes and the sea.

3 PRESENT STATUS OF LAKES IN SWEDEN - A GEOMORPHOLOGICAL REVIEW

3.1 Type of lake

A geomorphological lake register for Sweden has been set up (Håkansson et al 1983). About 1000 lakes are included in the register.

A lake can be classified in many ways, for example according to some of its morphometric data such as volume, area, depth etc. In a report (Håkansson 1978) about Lake Vänern many morphometric parameters are defined and described.

In the geomorphological lake register three morphometric base parameters have been used. They are lake area (A), lake volume (V) and maximum depth (D_{\max}). From these parameters it is possible to deduce other expressions, which describe the character of a lake.

Håkansson has used the following morphometric parameters:

- mean depth, $D_{\text{med}} = \frac{V}{A}$ (3-1)
- volume development, $VD = \frac{3 \times D_{\text{med}}}{D_{\max}}$ (3-2)
- the potential area of erosion and transport bottoms, $A_{\text{-ET}}$ (% of the total lake area).

The form of the lake (the relative hypsographic curve) is also defined by Håkansson. In Figure 1 five different lake types are represented.

Table 1 gives among other things the relation between the different classes and the volume development.

A very convex lake has shallow shores and only a small part of it is deep. The opposite lake type, concave, has steep shores and a large area within the same depth interval.

These different shore conditions are of great importance for sedimentation-resuspension, i.e. they may determine whether the lake has an erosion-transportation bottom or an accumulation bottom. In addition the depth conditions are very important for the biomass development.

Table 1. Terminology and classes for the different lake types
(from Håkansson 1981)

| Name | | Probability % | Classes | Volume development |
|-----------------|-----|------------------|-----------------|-----------------------|
| Very convex | VCx | 6.545 | f(-3)-f(-1.5) | 0.05-0.33 |
| Convex | Cx | 24.170 | f(-1.5)-f(-0.5) | 0.33-0.67 |
| Slightly convex | SCx | 38.300 | f(-0.5)-f(0.5) | 0.67-1.0 |
| Linear | L | 24.170 | f(0.5)-f(1.5) | 1.00-1.33 |
| Concave | C | 6.545 | f(1.5)-f(3) | 1.33-2.0 |

The area of erosion and transport bottoms (A_{-ET}) has been calculated from the following formula

$$A_{-ET} = 100 - A_{-ACK} = 25 \times \sqrt{A/D}_{med} \times 41^{0.061 \times D_{med} / \sqrt{A}} \quad (3-3)$$

where A_{-ACK} is the accumulation area (%)

If $\sqrt{A/D}_{med} = DR$ (dynamic ratio) eq (3-3) will become

$$A_{-ET} = 25 \times DR \times 41^{0.061/DR} \quad (3-4)$$

3.2 Geomorphological regions

The Nordic countries have been divided into 18 geomorphological regions (Rudberg 1968). Twelve of the eighteen regions are of interest in Sweden. From a cluster analysis (Håkansson 1983) it is clear that several of the regions show morphometric similarities. It is possible to obtain five lake classes, see Table 2.

Table 2. Lake classes

| <u>Lake class</u> | <u>Type of lake</u> |
|-------------------|------------------------------|
| 1 | Lakes in flat terrain |
| 2 | Lakes in hilly terrain |
| 3 | Lakes in very hilly terrain |
| 4 | Lakes in mountainous terrain |
| 5 | Lakes in fjeld terrain. |

The different regions are shown in Figure 2 (Håkansson 1983).

A table is also included in the Figure 2, showing the most probable volumes, mean depths and erosion-transportation bottoms for lakes having an area of 3 km². It is evident that the mean depth differs a lot between the five regions.

The lake classes have also been divided into three different area classes:

| | | |
|---|----|----------------------------|
| - | A0 | A < 1 km ² |
| - | A1 | 1 < A < 10 km ² |
| - | A2 | A > 10 km ² |

The distribution among the area classes (A0-A2) is roughly 60, 30 and 10 percent. The lake classes are dominated by class 3. About 70

percent of the 1060 lakes are found in this class.

To exemplify the distribution of lake parameters the class A0/3 has been chosen; statistics for this class are presented in Table 3.

Table 3 Geomorphological parameters of area class A0,-lake class 3

| | Area km ² | Volume km ³ | Max depth m | Mean depth m | Volume develop- ment |
|-----------------------|-------------------------|---------------------------|-------------------|--------------------|----------------------------|
| Mean | 0.237 | 0.00119 | 10.6 | 4.2 | 1.33 |
| Standard deviation | 0.249 | 0.00197 | 7.3 | 2.5 | 0.43 |

From Håkansson 1983.

Correlationcoefficients have been calculated for the different classes. These coefficients for class A0/3 are found in the table below.

Table 4 Correlation coefficients for class A0/3

| | |
|--------------------------------|-------|
| Mean depth - Max depth | 0.83 |
| Area - Volume | 0.77 |
| Mean depth - Volume | 0.72 |
| Max depth - Volume | 0.64 |
| Max depth - Volume development | -0.49 |
| Area - Max depth | 0.34 |
| Area - Mean depth | 0.32 |

From Håkansson 1983.

These values are representative for most of the classes.

4 COASTAL ZONE EVOLUTION

4.1 Sea level variations

An inland ice will by its weight press down the earth's crust. When the ice melts the crust begins to return to the original level before the ice age. This movement of the crust is called isostatic land uplift.

The inland ice contains great quantities of water in solid form. It has been calculated that during the last ice age about 35 to 40 km³ more water than nowadays was retained (Lundegårdh 1970). This is equivalent to a lowering of the sea level of 90 to 100 m. When the ice melted the sea level rose again. As long as melting inland ice exists, this so-called eustatic effect will diminish the regression of the sea level. There have been periods in southern Sweden when this effect has dominated and the shores have been submerged. This is called transgression of the sea level, i.e. the opposite of regression.

Because of these two opposite effects it is more appropriate to talk about shore displacement instead of land uplift. The shore displacement has been studied in many places along the Swedish coast. The displacement has been highest in Angermanland, around 285 meters. The shore displacement was very rapid in the beginning, around 10 cm/year (Miller 1982). However, the displacement decreased to about 2.5 cm/year during the Litorina stage of the Baltic, i.e. around 4000-7000 years B.P. During the last 3000 years the shore displacement has been around 1 cm/year. This present value decreases to

around 0.5 cm/year in the Stockholm area and is around zero in the southern part of Sweden.

It has been possible to use varved lake sediments to study the development of a lake from the time when it was isolated from the sea (Segerström, Renberg 1982). In the Umeå area the time of isolation has been obtained from sediment studies. For example Sarsjön, about 40 km north-west of Umeå, was isolated from the sea about 9000 years ago. Its height above sea level is nowadays 177 meters. Thus the mean shore displacement is around 2 cm/year.

There are certain conditions that must prevail to get the varved lake sediments. The changing seasons provide the necessary conditions to obtain varves with different thickness and colour. No stirring due to bioturbation or wave motion in the sediments may occur.

These still conditions at the bottom can be obtained in productive lakes with depths exceeding 6-7 meters (Segerström, Renberg 1982).

4.2 The Sibbofjärden and Trobbofjärden area

In the vicinity of Studsvik there are two enclosed seas, Sibbofjärden and Trobbofjärden. They are typical examples of the development of archipelago areas in Sweden.

4.2.1 Description of the Sibbofjärden

Sibbofjärden is nowadays an enclosed sea, but over the next few hundred years it will be isolated from the sea and become a lake with fresh water. Its threshold at the outlet is around 1-1.5 m below the mean sea level.

The "lake" area is 5.6 km^2 and the drainage area is 83 km^2 . The area of arable land is 25 percent of the total area. This part of the drainage area is the former sea bottom of the bay. The calculated "lake" volume is $2.6 \times 10^7 \text{ m}^3$ and the mean depth is almost 5 m. In the table below some morphometric data are presented.

These data are calculated according to Håkansson (1978).

Table 5 Morphometric data of Sibbofjärden

| <u>Parameter</u> | |
|--|----------------------|
| Area | 5.6 km^2 |
| Volume | 0.026 km^3 |
| Mean depth | 4.7 m |
| Maximum depth | 11 m |
| Relative depth | 0.4 m |
| Maximum length | 6.0 km |
| Mean width | 0.9 km |
| Area of erosion and transportation bottom | 20.8 % |
| Dynamic ratio | 0.5 |
| Volume development | 1.3 |

4.2.2 Residence time for Sibbofjärden

The total volume of Sibbofjärden is 0.027 km^3 . A specific discharge of 5.5 l/s km^2 (Tryselius 1971) and a catchment area of 83 km^2 give a theoretical residence time of 1.7 years.

However, the bay is connected with the sea, i.e. it has a water exchange through the outlet. A rough estimate of this exchange gives a value of $3 \times 10^7 \text{ m}^3/\text{y}$. This is equivalent to a residence time of around 285 days. The two sources of water exchange for the bay give together a total residence time of around 200 days.

To obtain the exchange through the outlet the water fluctuations and their duration and amplitude (reduced) in Tvären has been used.

To get a better understanding of the water exchange, especially through the outlet it is necessary to measure the flux by current meter during some representative periods.

4.2.3 Field survey in March 1984

In March a survey in the areas of Sibbofjärden and Trobbofjärden was performed, see Figure 3. The following parameters were measured at seven places in Sibbofjärden and at one place each in Trobbofjärden and Rundbosjön respectively;

- depth
- conductivity (salinity)
- pH
- temperature
- ice thickness

In addition, sediment cores were taken at the same places.

The depth in Sibbofjärden varied between 2 and 5.5 m. In order to obtain a more exact measure of the volume it would be necessary to take soundings over the whole bay.

The variation of the conductivity with depth and distance from the outlet is shown in Figure 4. In the surface water (0-2.5 m) below the ice a halocline exists. This means that the water below the halocline is brackish with increasing conductance towards the bottom.

In the fresh surface water a slight decrease with increasing distance from the outlet can be

seen. The opposite situation is valid for the bottom layers. The bottom value is around 650 mS/m. This can be compared to the value of 725 mS/m outside Sibbofjärden.

The pH varies between 5.60-7.25. The highest values are obtained at the bottom. No special gradient is found. In the vicinity of the inlet at Björksund the pH is somewhat higher in the surface layer. This depends on the discharge from arable land areas, which usually have a higher pH.

The temperature varies between 0.4 to 2.2°C in Sibbofjärden from the surface to the bottom.

The temperature in the northern part, Sundhällafjärden, deviates from that of Sibbofjärden proper, with a higher temperature at the bottom. This is around 4°C.

The ice thickness was around 40 cm on the whole of Sibbofjärden.

One measuring point in the southern part of Trobbofjärden was included in the survey to compare the two enclosed seas. In 1957 a dam was built at the outlet of Trobbofjärden to regulate the inflow from the Baltic. The whole of Trobbofjärden was converted to a freshwater reservoir over a few years.

An additional site was chosen in Rundbosjön, a lake within the catchment area of Trobbofjärden. It was isolated from the sea around the Viking Age, i.e. about 1000 years ago.

The specific conductance in Trobbofjärden varied between 21 and 32 mS/m, from the surface to the

bottom at 2 m. In Rundbosjön the corresponding values were 16 to 24 mS/m at 8 m depth.

The pH values were around 6 for both lakes.

The temperature at the bottom (2 m) of Trobbofjärden was 2.6°C and in Rundbosjön at 8 m depth it was 5.0°C.

4.2.4 Field survey in June 1984

A survey in the beginning of June 1984 showed that Sibbofjärden had a marked temperature stratification. The thermocline was very strong between 5 to 6 meters, about 8°C per meter. A vertical section from the deepest part of the "lake" is shown in Figure 5.

The halocline was found between 5 and 7 meters, see Figure 5. In the epilimnion (surface water) the conductivity was just below 500 mS/m. These values are comparable with values found at the 2 meter level during the winter survey. Below 7 meters the conductivity was around 700 mS/m, comparable with the conductivity found outside Sibbofjärden at Helgö.

From the two surveys it is evident that the salinity (conductivity) in the bottom layer is the same as in the sea outside Sibbofjärden. Further, there is no marked horizontal stratification of the salinity. The salinity is about the same at the outlet as in the northernmost part of the enclosed sea. This is valid for the epilimnion as well as for the hypolimnion (the bottom water below the thermocline).

Depth measurements gave a maximum depth of around 11 meters.

4.3 Other coastal areas of interest

Two areas will be mentioned here, Utålskedjan in Uppland and a coastal area close to Umeå. There are of course other sites that can be of interest. However, these two are examples of the development of coastal areas from brackish sea to freshwater lakes.

Utålskedjan is a chain of lakes with increasing salinity towards the Baltic (Ingmar and Willén, 1980). A comprehensive material covering topography, sediment, vegetation, hydrology, water chemistry etc was collected during two periods, 1953-61 and 1967-75.

The innermost part of the catchment area was isolated during the Middleages. Some lakes are freshwater systems for the greater part of the year. The thresholds are below the high-water level, which means that brackish water can enter the lakes.

The different sediment layers originating from the brackish and freshwater periods respectively have been studied. The marine clay gyttja with a low content of organic material (10-15 %) can be distinguished from clay gyttja with a higher organic content. The depths of the sediments are roughly between 5-10 m. The sedimentation velocity in the deepest parts is 3-7 mm/year.

In the Umeå area the varved sediments have been studied, as mentioned earlier (Segerström, Renberg 1982). The consequences of the land uplift on the vegetation development in the coastal zone in the vicinity of Umeå have also been studied (Ericsson 1982).

5 THE TIME SCALE OF LAKE EVOLUTION

The sedimentation rate is not constant. It varies according to the climate, bioproduction etc as has been mentioned above. An example of this is found in Figure 6, showing the sediment growth from Lake Trummen (Lettevall 1973).

The sedimentation varies within a lake, with the highest rates in the deepest part of the lake. This is illustrated in Figure 7.

An example from Poland (Pawlikowski et al 1982) shows lake development during the last 12000 years, see Figure 8. In this figure a cross section of the sediments of an overgrown lake at Woryty is shown. There are different layers with peat and gyttja from different stages of the lake development. Nine different stages have been identified. The sedimentation velocity has varied between 0.3 and 1.6 mm/y.

The sedimentation velocity in Swedish lakes varies within the range 0.5-8 mm/y (Håkansson 1981). A value around 2-3 mm/y can be reasonable to use for calculations. The compaction is included in this value.

A theoretical calculation of the silting up for different lake types has been done. Three different types, very convex, slightly convex and concave, have been used.

A constant sedimentation over the whole lake area is assumed. The calculations are presented in Figure 9. It can for example be seen that when the depth has been reduced to half of the initial value, the remaining lake volume is 35, 15, and 7 percent of the original for the

concave, slightly convex and the very convex lake types respectively.

It is also interesting to study how the lake areas change with decreasing depth for the different lake types. These variations are shown in Figure 10. The differences between the lake types are great. For example, for a depth reduction of 25 percent the remaining lake area is 95, 60 and 15 percent for concave, slightly convex and very convex type lakes respectively. These differences are of importance for biomass development in the littoral zone.

To be able to calculate the concentration of for example, an element entering a lake, the residence time in the lake must be known. To illustrate how the silting up affects the residence time for different lake types, a lake of the size of Sibbofjärden has been chosen. The discharge is that of the catchment area for Sibbofjärden ($5.5 \text{ l/s}\cdot\text{km}^2$). The sedimentation is 2 mm/y , and the maximum depth is 10 m . This means that it will take 5000 years to fill up the lake, if conditions are constant over the whole period. The results of the calculations are shown in Figure 11.

The residence time varies according to the runoff, catchment area and lake volume. An attempt has been made to find the limits for the residence time.

The average annual runoff varies between 4 and $50 \text{ l/s}\cdot\text{km}^2$. The low values are found in the south-eastern part of Sweden and the high values are obtained in the high mountain areas (Tryselius 1971). Sweden can be divided into nine hydrological regions (Melin 1980), see Figure 12. The

monthly river runoff from these different regions has been studied (Gottschalk 1975). The average annual runoff within these regions varies between 8 and 20 l/s·km². However, the monthly runoff can vary as much as from 2 to 90 l/s·km² within the same region.

In order to calculate the discharge from runoff values, the catchment area must be determined. As the lake areas are known from the geomorphological register, one way is to calculate the catchment area from the lake percentage and lake area. The lake percentage for the different regions has been calculated from areas exceeding 200 sq km (SMHI 1970). In Table 6 the values used are presented.

For the calculation of the residence time the mean lake percentage has been used for each region. In addition, a main lake type has been chosen for each region. The residence time is calculated for the three area classes for each lake type. The results are given in Table 7.

Table 6 Runoff and lake percentage area

| Region | Runoff (l/s·km ²) | | | Lake percentage (%) | | |
|----------------|-------------------------------|-----------------|-----------------|---------------------|---------|---------|
| | Annual Mean | Monthly Maximum | Monthly Minimum | Mean | Maximum | Minimum |
| A | 17 | 60 | 3 | 4 | 13 | 1 |
| B | 20 | 90 | 2 | 8 | 16 | 2 |
| C | 17 | 73 | 3 | 8 | 16 | 2 |
| D | 17 | 72 | 2 | 6 | 12 | 1 |
| E | 11 | 36 | 2 | 5 | 8 | 3 |
| F _a | 8 | 15 | 2 | 9 | 15 | 1 |
| F _b | 14 | 23 | 5 | 6 | 14 | 0 |

Table 7 Residence time for different hydrological regions and lake types

| Region | Lake type | Residence time (years) | | |
|----------------|-----------|------------------------|---------------------------|-----------------|
| | | Area < 1 sq km | 1 sq km < Area < 10 sq km | Area > 10 sq km |
| A | 1 | 0.2 | 0.3 | 1.9 |
| B | 4 | 0.6 | 1.4 | 3.0 |
| C | 3 | 0.7 | 1.2 | 3.2 |
| D | 3 | 0.6 | 1.0 | 2.9 |
| E | 2 | 0.4 | 1.0 | 0.6* |
| F _a | 3 | 1.8 | 3.1 | 8.4 |
| F _b | 3 | 0.7 | 1.2 | 3.3 |

* only 4 lakes are included in this class

Another method of calculation, using data from the Swedish geomorphological lake register, will be presented below. Three different classes, A0-3, A1-3 and A2-3, representing about 70 percent of the lakes within the register, have been chosen. The mean depths for the different classes are used to calculate the theoretical lifetime of the lakes. To simulate an increased sedimentation because of increasing organic production at the end of the life of the lake, different sedimentation rates are used for different depth intervals. The sedimentation rates are 3 mm/y for 0-2 meters, 2 mm/y for 2-5 meters and 1 mm/y for depths over 5 meters.

The results from the calculations of the time before the lakes are filled up with sediments are presented in Table 8. The 95 % confidence levels given are only calculated from lake data. No attempt has been made at this stage to evaluate the uncertainty of the sedimentation rates.

Table 8 Theoretical lifetimes for different lake classes

| Class | Mean depth m | Standard deviation, m | Lifetime years |
|-------|-----------------|--------------------------|-------------------------|
| A0-3 | 4.2 | 2.5 | 1800 ₊ 100 |
| A1-3 | 7.7 | 4.2 | 6000 ₊ 500 |
| A2-3 | 14.6 | 10.2 | 13000 ₊ 3000 |

These calculations will give the magnitude of the remaining lifetime for the present lakes. However, the calculations can be modified to allow for different sedimentation rates at different depths, the vegetation in the littoral zone, bioproduction within the water mass etc. These different parameters and their variations must be included in future studies.

6 CONCLUSIONS

Most of the recent lakes in Sweden were originally formed by the latest inland ice. However, the lakes are occasional phenomena. Many processes affect the evolution of a lake. Some of these are discussed in this report.

Lake evolution goes through several stages, where the relative importance of the different processes will change.

The water is the carrier system for suspended material, dissolved substances, biomass etc. Because of this it is important to know the residence time during different stages of lake evolution.

The sedimentation is also dependent on the water transport to and within the lake. The little known relation between sedimentation rate and residence time must be determined, so as to be able to find the transfer coefficients between water and sediment, and their variations. The water transport also affects the horizontal and vertical distribution of the sedimentation.

Another important parameter is the stratification of the lake, mainly the thermal stratification. A reduced vertical water exchange will for example affect the oxygen condition at the bottom.

In the coastal areas the transition from brackish water to fresh water produces differences from the pure lake systems as regards stratification, sedimentation etc. Because of this the transition period must be treated separately when dealing with lake evolution. The Sibbofjärden-Trobbofjärden areas are suitable for studying these differences.

In order to realize a program for lake, bog or bay evolution for the Sibbo-Trobbofjärden area, a field survey must be carried out over some years. This is required for two principal reasons, firstly to acquire a knowledge of the systems and secondly to collect soil, water, vegetation and sediment for laboratory studies.

Such a field survey will include water and material balances, sampling of soil and sediment, measuring of sedimentation rate and the estimation of pH and Eh in the field.

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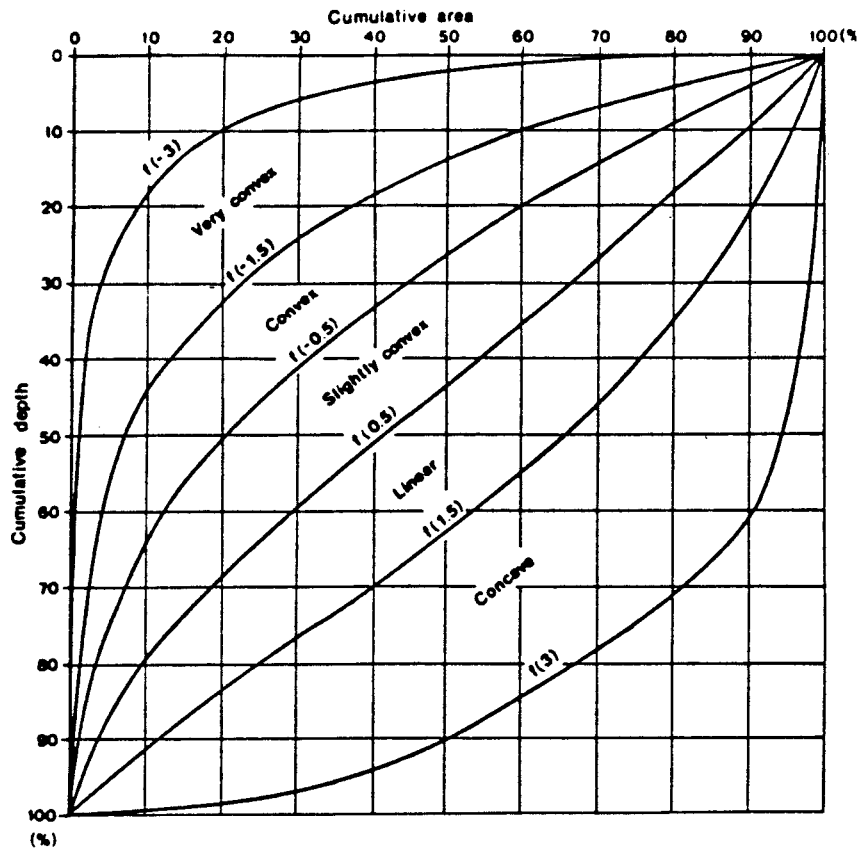


Figure 1. Relative hypsographic curves for the statistical lake forms. From Håkansson (1983).

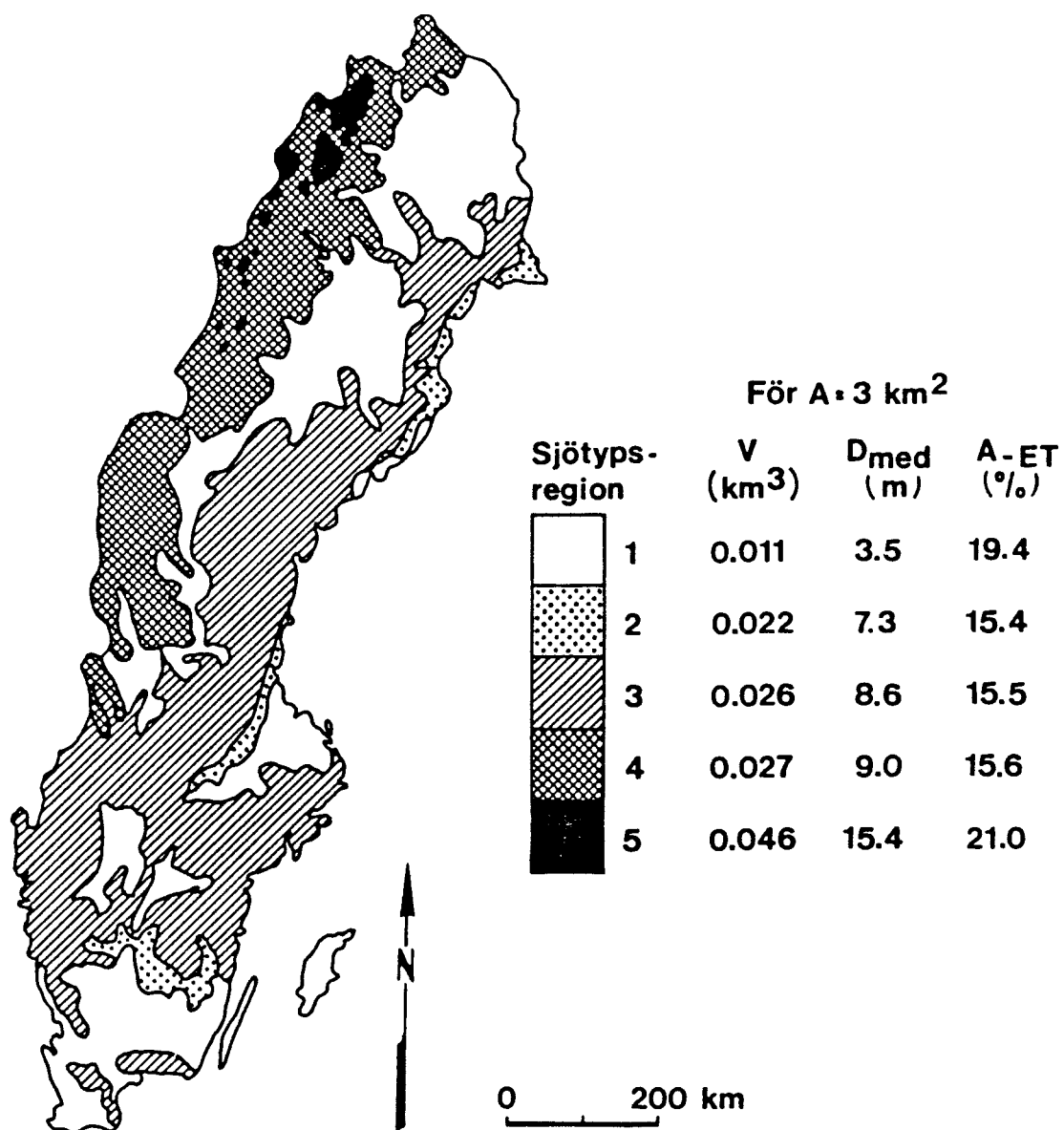
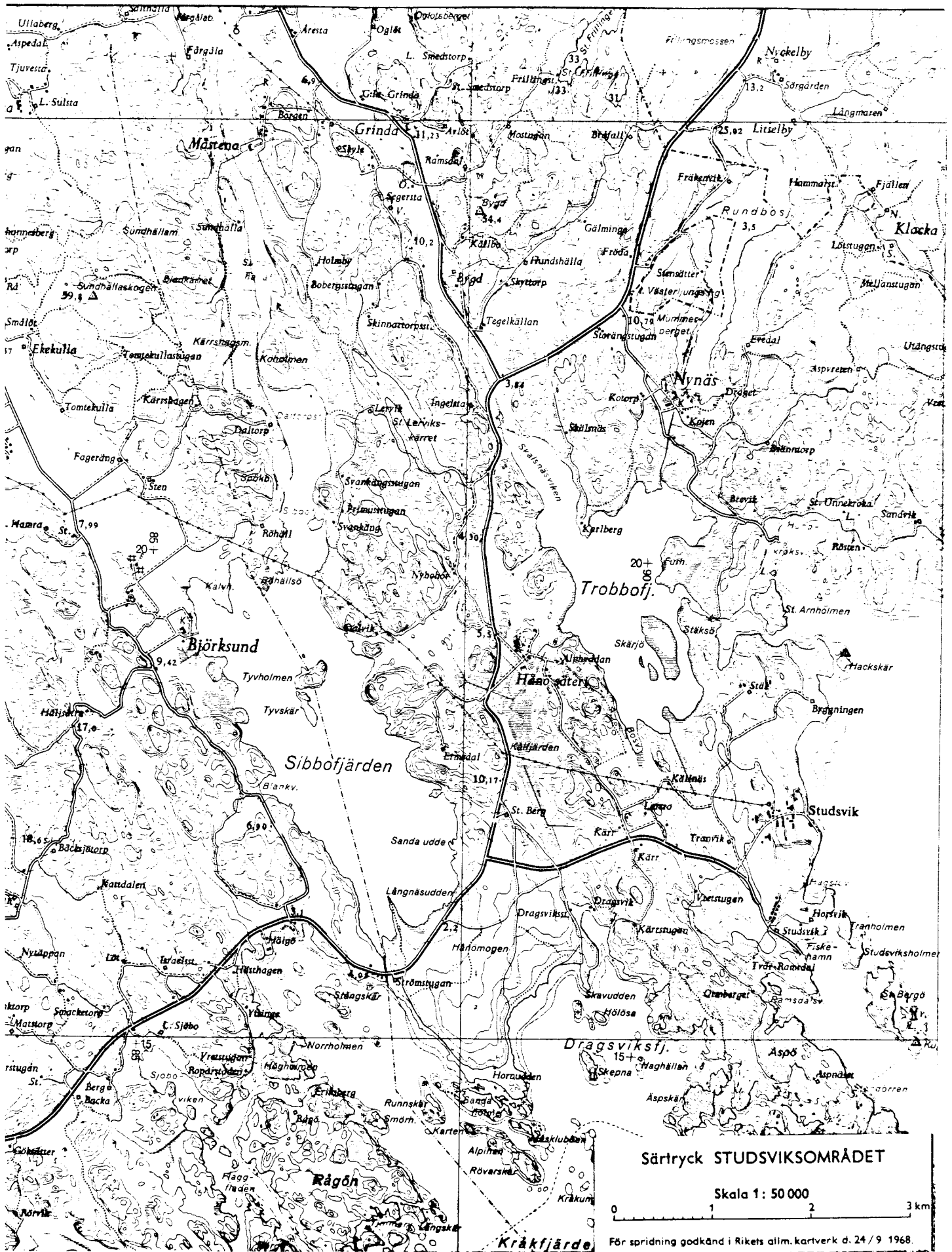


Figure 2. Geomorphological lake regions.
From Håkansson (1983)



Särtryck STUDSVIKSOMRÅDET

Skala 1: 50 000



För spridning godkänd i Rikets allm. kartverk d. 24/9 1968.

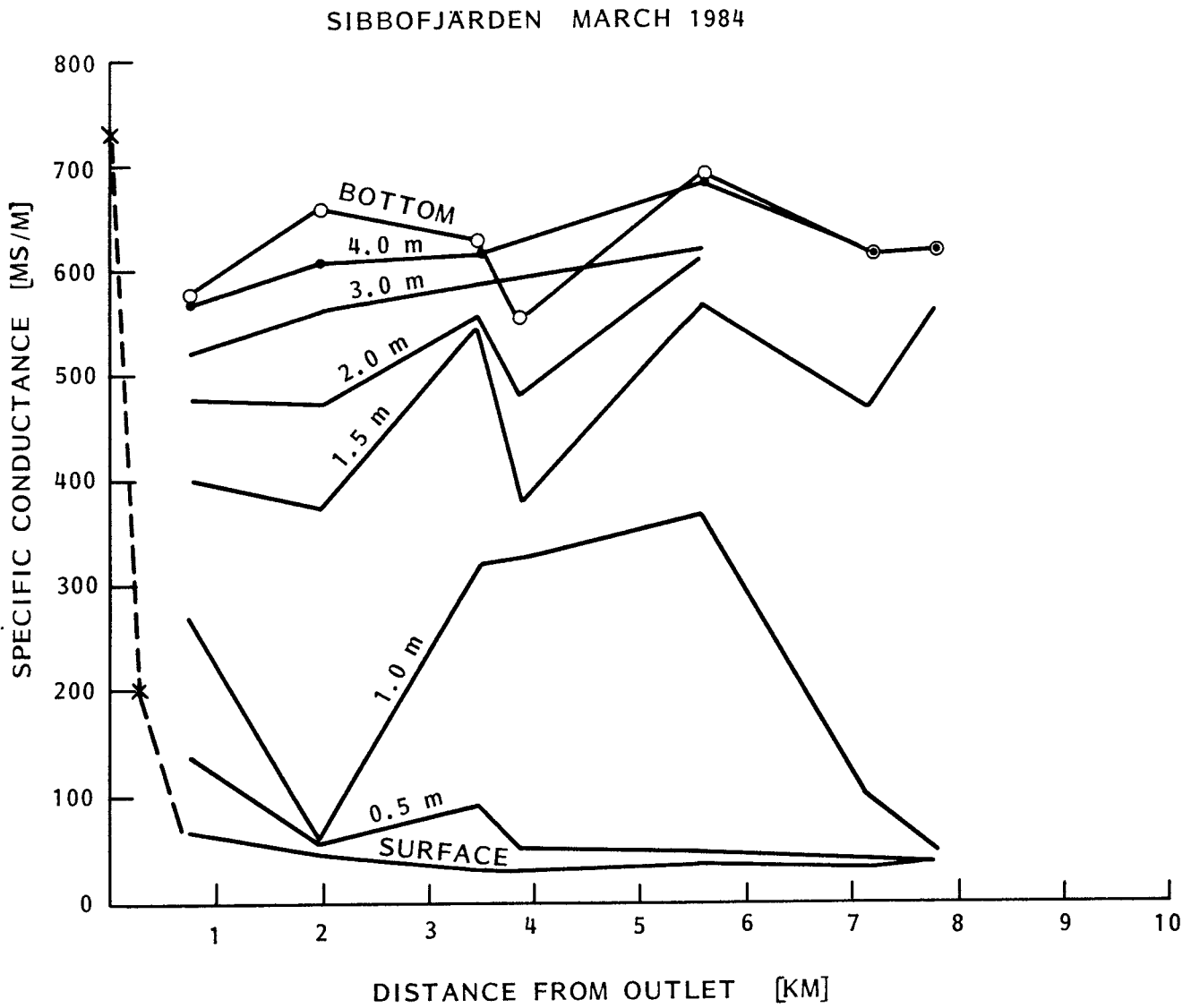


Figure 4. Conductivity in Sibbofjärden in March 1984.

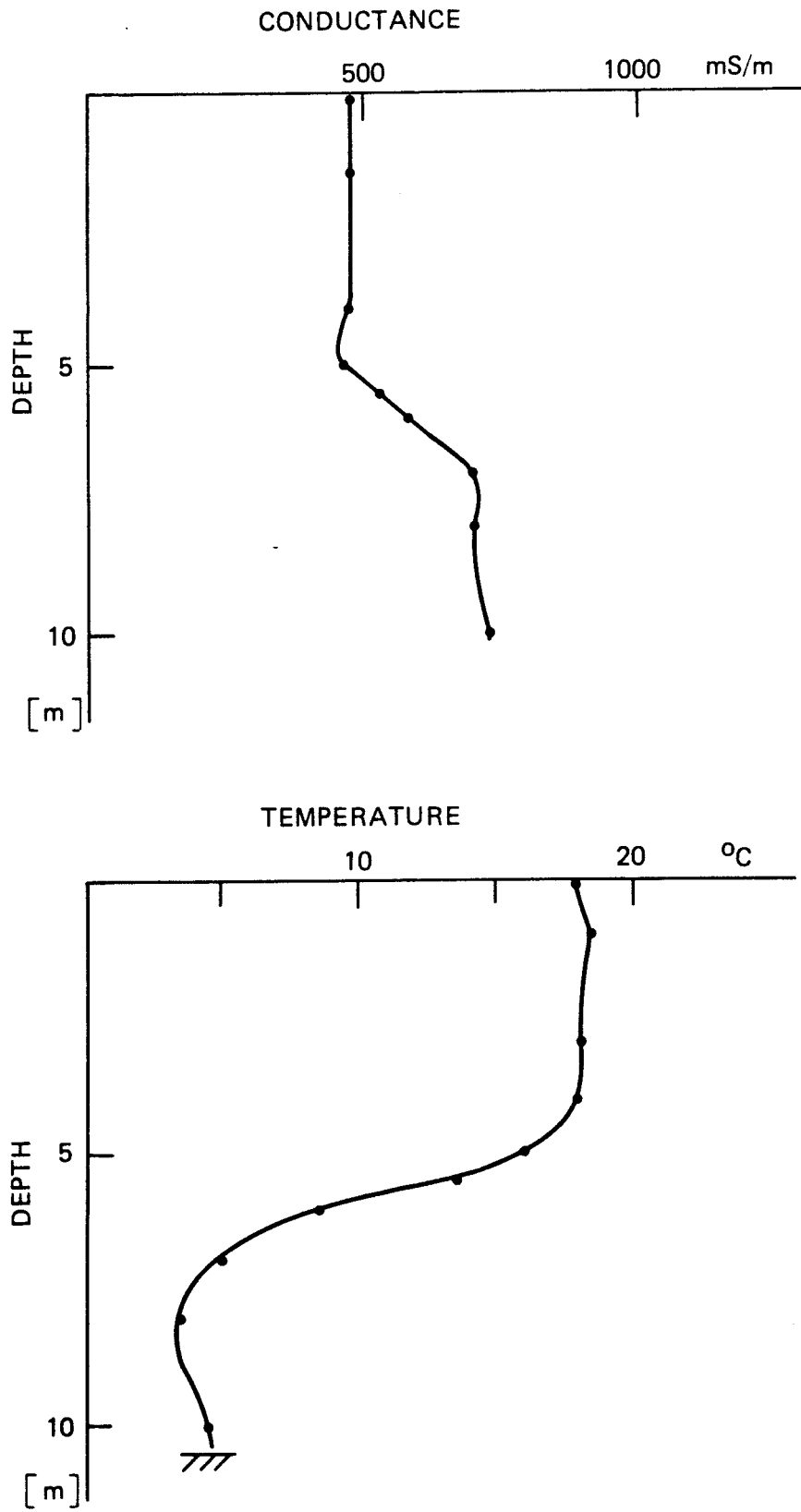


Figure 5. Conductivity and temperature in Sibbofjärden in June 1984.

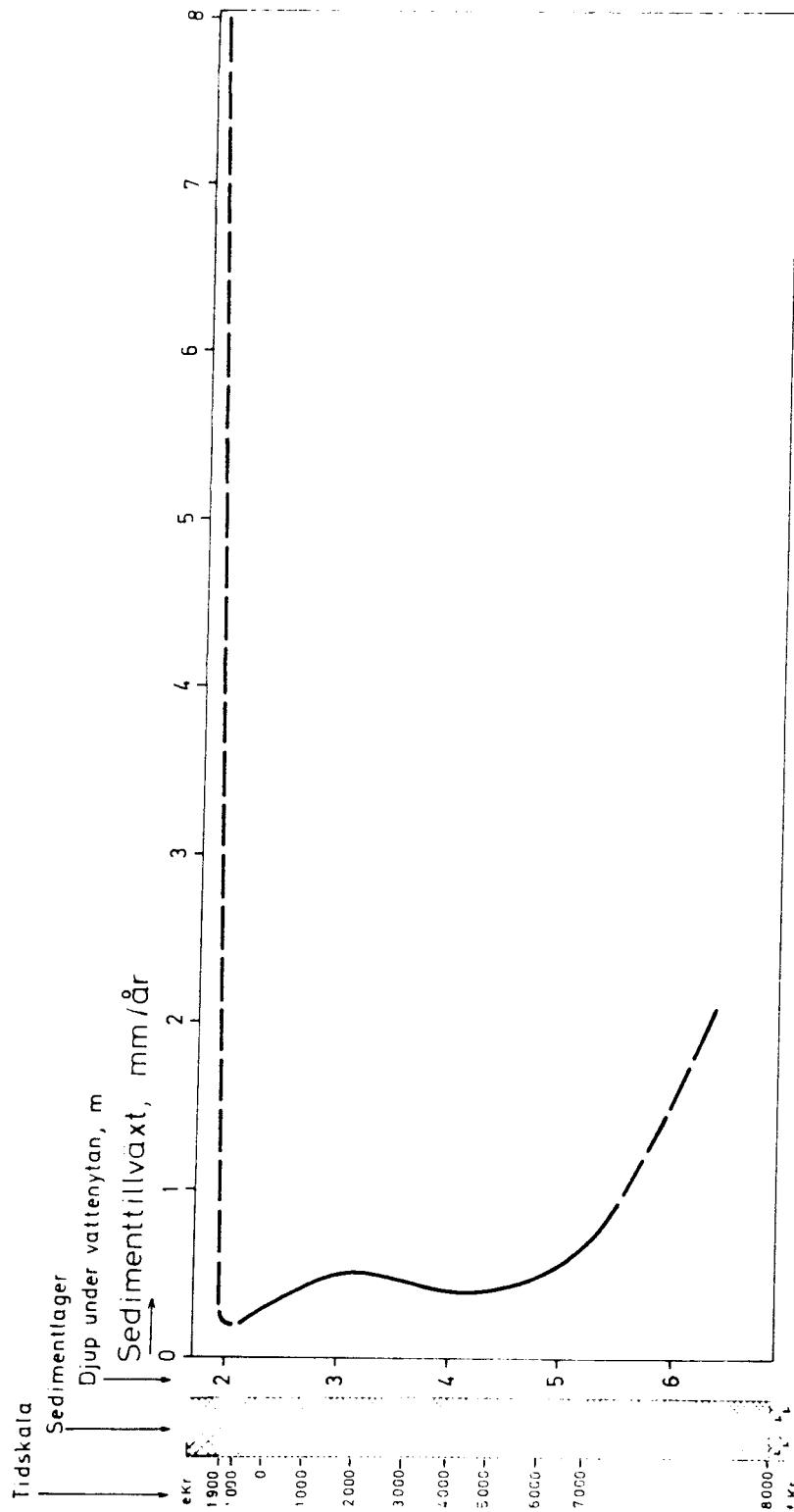


Figure 6. Sedimentation rate in lake Trummen.
From Lettevall (1973).

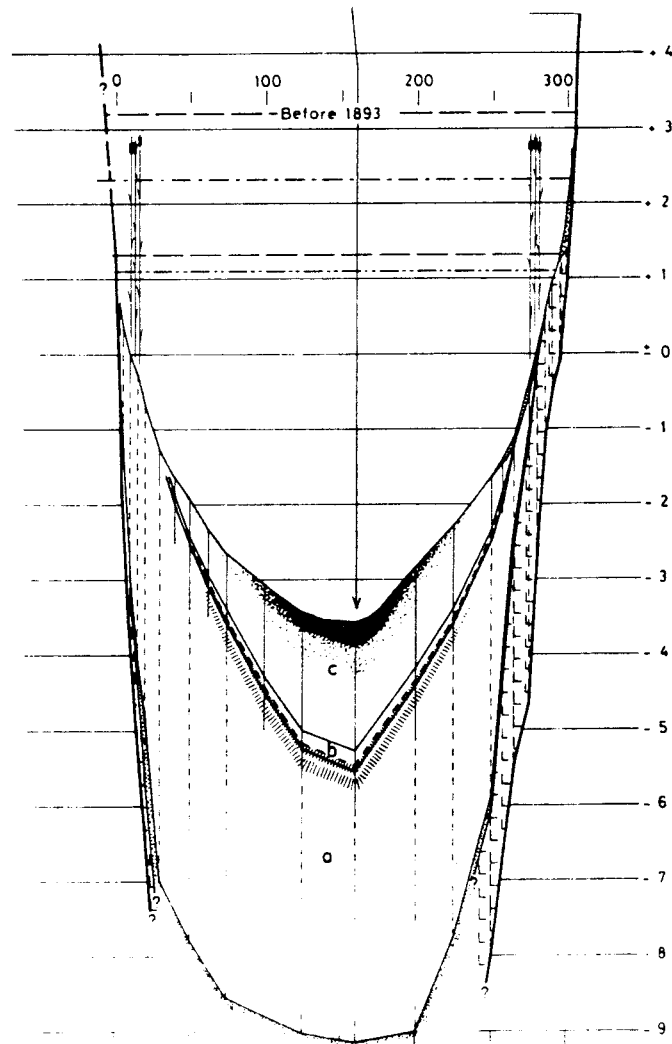
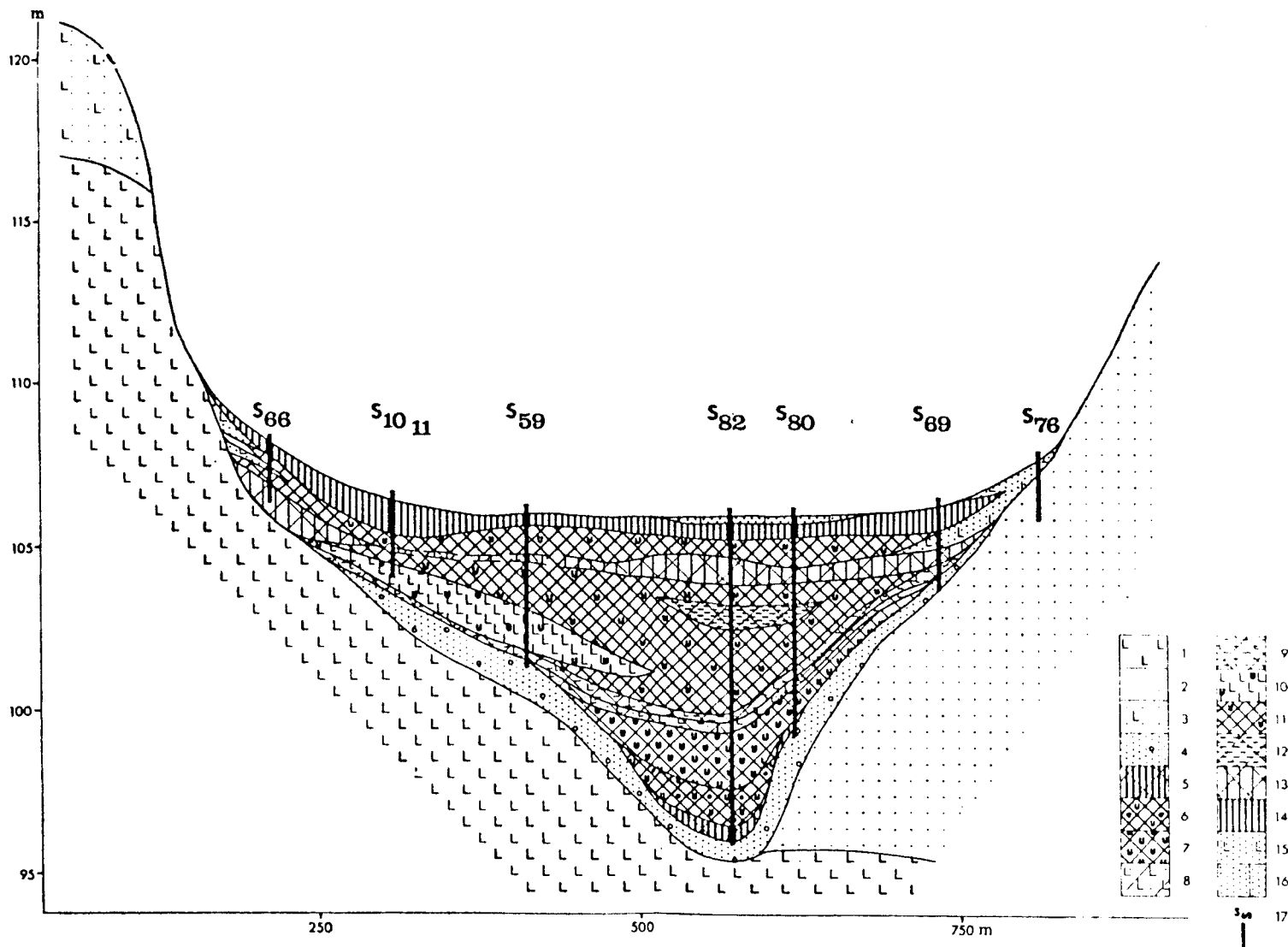


Figure 7. Sediments in the Utål chain basins. Depths in meters. a = normal "marine" clay-gyttja, b = clay-gyttja or gyttja organic content 20-35 %, c = as "b" with less saturated colours. From Ingmar, Willén (1980).

Figure 8. Sediment structure.
From Pawlikowski (1982).



Section across the Woryty site along the A—B transect shown in Fig. 3 (symbols follow Troels-Smith, 1955):
 1 — glacial till, 2 — fluvio-glacial sands, 3 — kame silts and fine sands, 4 — coarse sands with gravel, 5 — basal peat, 6 — ferruginous gyttja, 7 — calcareous gyttja, 8 — sandy silt with gyttja, 9 — dy-like sediment, 10 — calcareous silt, 11 — fine detritus gyttja with variable carbonate content, 12 — spropel-like sediment, 13 — swamp peat with gyttja, 14 — surface peat, 15 — slope land-slide material deposited in the marginal zone of lake, 16 — surface sands, 17 — position of corings, S-82 and S-80 sampled for paleoecological investigations

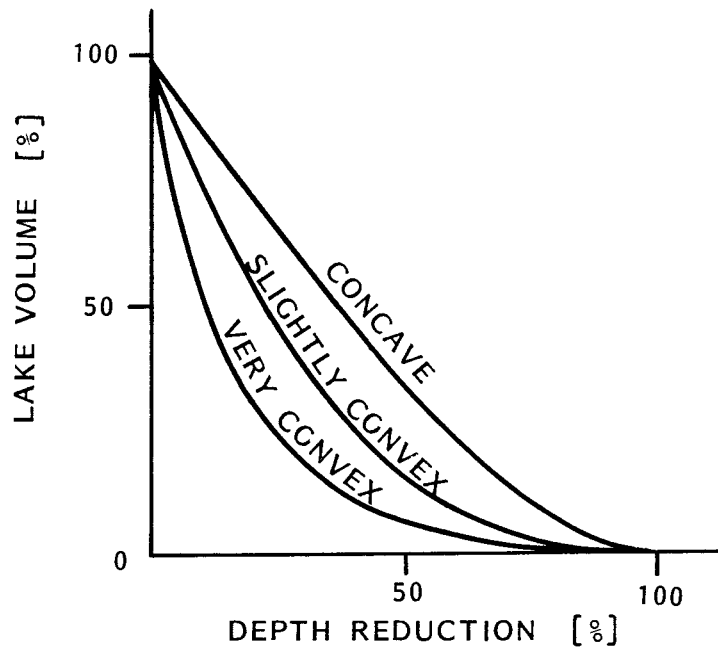


Figure 9. Depth-volume relations for different lake types.

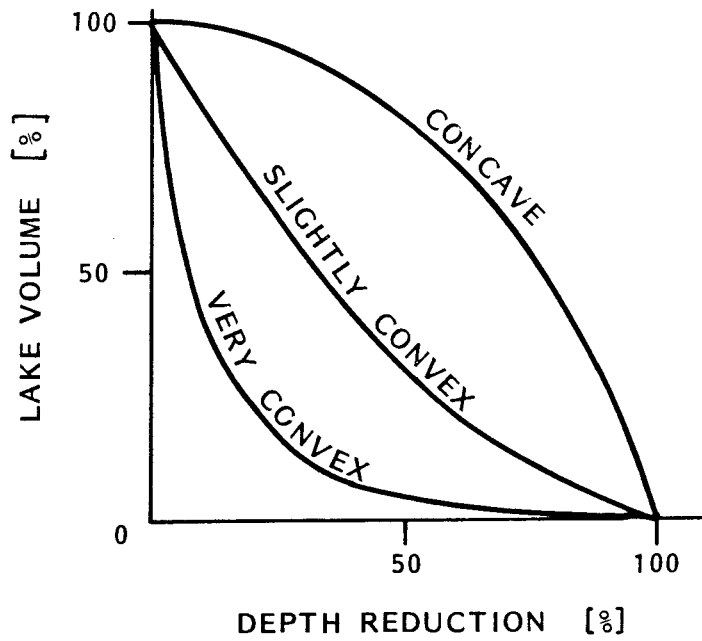


Figure 10. Depth-area relations for different lake types.

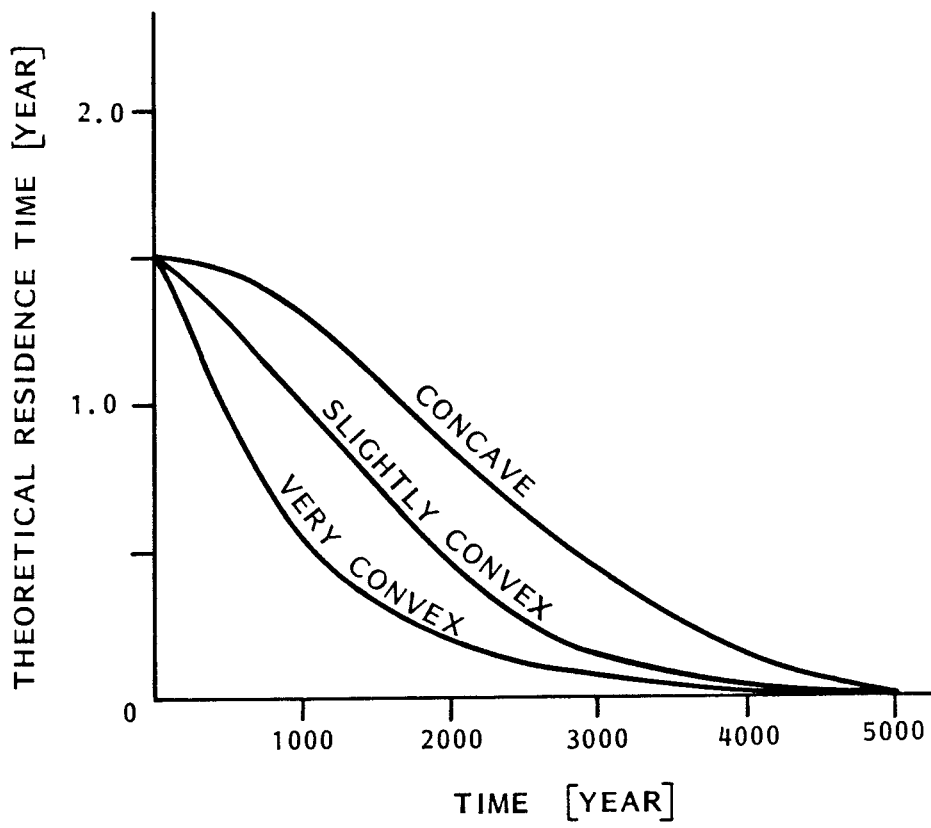


Figure 11. Theoretical residence time for different lake types.

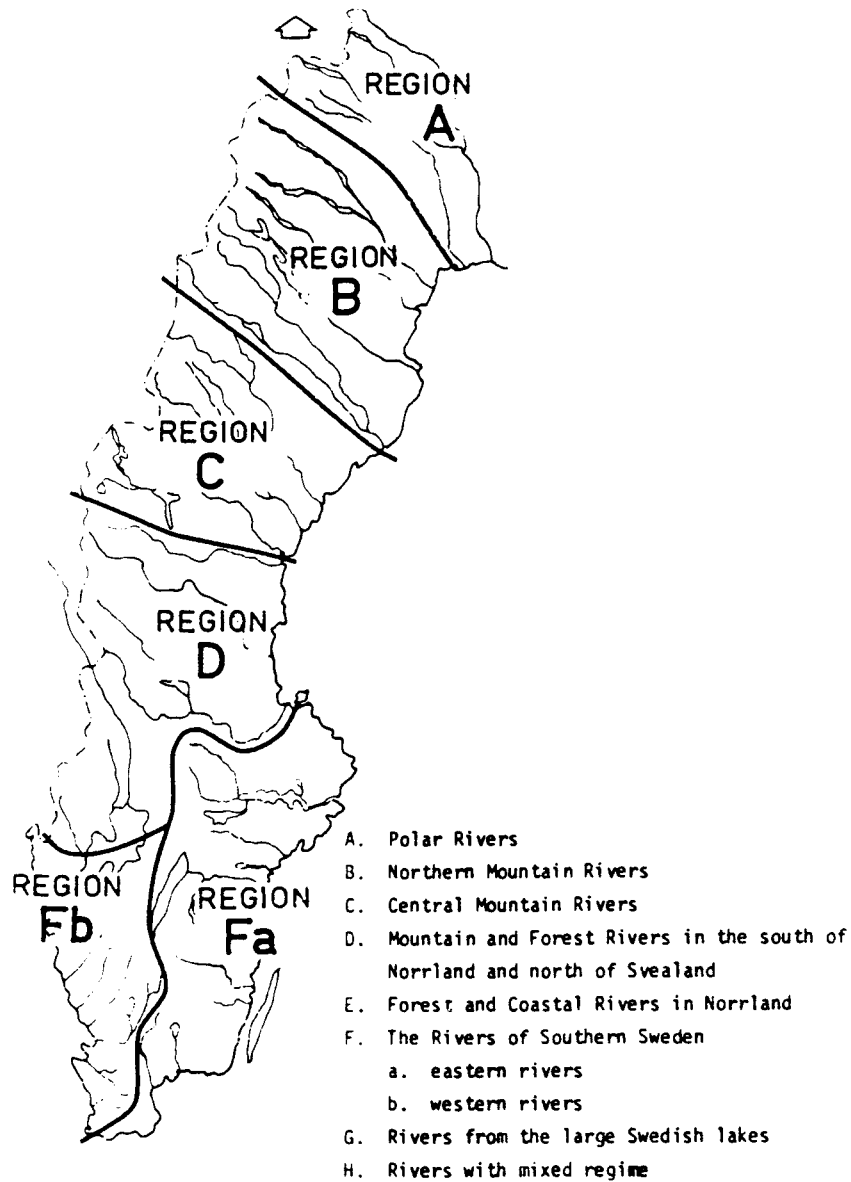


Figure 12. Hydrological regions according to Melin (1970).

1984-07-20

P O Agnedal

THE AGEING OF A LAKE - CHANGES IN PLANT AND
ANIMAL LIFE

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FIGURES

1 INTRODUCTION

A lake is not a stable formation but changes during its life. Depending on the conditions of its surroundings, it develops either into arable land or into a peat bog.

Each step in this development has a character of its own and the duration of each step can be very different, but mostly the changes accelerate towards the end.

The geo-morphological development of a lake is described in another report /1/. Irrespective of how a lake is formed it is initially poor in nutrients. An exception, however, is when a sea-bay, already rich in nutrients, is cut off from the open sea.

A lake in an area that is rich in nutrients normally ends up as arable land, but if it is very rich in nutrients the silting up can proceed very rapidly and the result can be a rich fen which later develops into a peat bog consisting of sedge and moss peat. If on the other hand the lake is situated in an environment of primary rocks and with no or little supply of nutrients, it is influenced by the surrounding woods and develops into a dystrophic lake and later to a peat bog.

2 CHARACTERISTIC FEATURES OF LAKE TYPES

All the relevant types of lake can be found in Sweden, and it is therefore possible to describe the different stages in the development by using existing lakes as examples. The oligotrophic lakes are found in the northern part of Sweden in the mountainous area, and also in the primary rock areas in southern Sweden.

The eutrophic lakes are situated in rural areas which mostly coincide with a background rich in natural nutrients, but they also occur where a poor environment is influenced by man.

The dystrophic lakes belong to areas surrounded by moors or pine forests and situated in primary rocks.

2.1 Water chemistry

2.1.1 Oligotrophic lakes

These lakes are most often clean and deep and the shores are steep or narrow which prevents rooted vegetation. The epilimnion is small compared with the hypolimnion. The water has a low conductivity due to the low concentration of major constituents such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , CO_3^{2-} , SO_4^{4-} and Cl^- . The turbidity is also low because of the small amount of plankton. It can however increase owing to clay particles or other allochthonous material.

The concentration of nitrogen and phosphorous is low in oligotrophic lakes, which gives a low production of phytoplankton. The oxygen content in the water is high from the surface to the bottom over the whole year, as the amount of organic material on

the bottom is small and there is a low demand for oxygen for decomposition.

2.1.2 Eutrophic lakes

In eutrophic lakes the concentration of major constituents is high and normally calcium is the dominant cation. The conductivity is therefore higher. There is also a transport of nitrogen and phosphorous to these lakes from the surroundings, but as they are situated in populated areas they also receive waste water and drainage water from agricultural areas.

The oxygen concentration in the water of a eutrophic lake varies during the year. A high phytoplankton production in the summer will create oversaturated conditions in the epilimnion and a deficit - sometimes no oxygen at all - in the hypolimnion due to the high decomposition rate of sedimenting organic material.

With the turn over in spring and autumn oxygen is transported to the bottom water, but during the stagnant period in the winter the oxygen is consumed by decomposition.

During the periods with oxygen deficit in the bottom water phosphorous is fixed in the sediment, but it will be this is released when the oxygen concentration increases. The transport of phosphorous to the upper photic zone makes a new production of phytoplankton possible.

The acidic precipitation during the last decades has changed the pH values in many lakes in Sweden, especially on the west coast and in areas with primary rocks i.e. lakes with natural low buffering capacity. It has been shown that the

decreasing pH-values change the conditions in the lakes in such a way that elements e.g. Al and U can be released from the bottom sediment.

Eutrophic lakes are not, however, as vulnerable as oligotrophic ones because of the high alkalinity values and high buffering capacity due to the high concentration of calcium.

2.2 Phytoplankton

Lakes can be classified not only from a chemical point of view but also from the species and composition of phytoplankton.

In an oligotrophic lake the amount of plankton is small, but it can be found not only in the upper layer but also in deeper water. In a eutrophic lake the presence of phytoplankton is limited to the upper layer, at least during the summer.

Green algae dominate over blue-green algae in an oligotrophic lake while in a eutrophic one the condition is reversed.

The seasonal variation of phytoplankton depends on factors such as i.a. temperature, light and nutrients. In the spring when the light increases, already below the ice a very rapid increase in the biomass - most by diatoms - occurs resulting in a water-bloom. This is an effect of the vertical mixing which has transported i.a. phosphorous to the surface layer; other elements have also reached their maxima at this time. The dead phytoplankton settle and some are decomposed before reaching the metalimnion, while others settle on the bottom. In the first case the nutrient will remain in the photic zone and can be used again, whereas in the second case the

nutrients are bound to the sediment until the next vertical mixing.

On account of the low concentration of nutrients during the summer the standing crop of phytoplankton is rather low. After autumnal vertical mixing a new maximum of phytoplankton can occur. This bloom is normally not as large as that in the spring because of the smaller amount of light and a transport of cells from the photic zone due to circulation. One notable observation is that, according to many investigations, the biomass of nanoplankton is larger in oligotrophic lakes than in eutrophic ones. It has also been found that with increasing eutrophication, the size of the phytoplankton increases /2/. Increasing eutrophication also lead to a change in the composition of phytoplankton species. (Fig 1).

2.3 Rooted vegetation

The presence of rooted vegetation in a lake depends both on the formation of the shore line and the bottom material in the trophogenic zone. The vegetation is also different on wind exposed shores compared with sheltered areas.

As already mentioned, oligotrophic lakes very often have shores that slope more abruptly and the area of rooted vegetation is therefore rather small. In the shallower eutropic lakes the bottom configuration is different and the area available for rooted vegetation is much broader (fig 2). On a wind exposed shore there will be an erosion of the bottom material which is transported to deeper areas, where sedimentation of fine material takes place. Between these two zones there is a neutral zone where sediment is collecting at the same rate as erosion occurs.

These circumstances are important for the possibilities of plants becoming rooted in the different areas.

Emergent plants like Phragmites and Typha can also exist on exposed shores and Ph. can grow in soil above the water surface and down to about 2 m depth. Typha is more easily injured by wind and waves and is therefore more often found in sheltered areas. Outside the zone of emergent plants one will find floating-leaved plants such as Nymphaea and Nuphar and also Potamogeton natans. These plants are rooted in sediment and can thus only live in areas where the bottom is stable enough and contains organic substances.

In deeper water the rooted vegetation consists of submerged plants such as Myriophyllum and Ceratophyllum. In the erosion zone in an oligotrophic lake the rooted vegetation is characterized by species of Isoetes, Lobelia and Litorella (fig 3).

The depth to which the vegetation extends depends i.a. on the light conditions, but most often mosses are the plants living at the greatest depth. (*Fontinalis antipyretica*, *Drepanocladus*).

The zonation of the vegetation in a fairly typical eutrophic lake is shown in figure 4.

2.4 Bottom fauna

As a result of changes in the chemical conditions and the spread of vegetation, the bottom fauna also changes in the evolution from oligotrophic to eutrophic conditions.

Of primary importance is the oxygen condition. If the oxygen concentration is high and there is no deficiency in the bottom water the bottom fauna is characterized by species demanding high oxygen concentrations like Tanytarsus /3/. The fauna is also rich in species and the biomass is relatively large.

In a eutrophic lake the bottom water can have an oxygen deficit during stagnation periods which prevents species with high oxygen demand from existing in this biotope. The fauna is therefore poor in species but the biomass is large.

According to Thienemann the above fauna is denoted a chironomid-fauna, being named after the most prevalent species.

One animal always present in such lakes is the Corethra larvae which is the only planktonic living insect-larvae in our lakes. With increasing vegetation in the littoral zone a good shelter and a good food supply is developed which increases the biomass of the bottom fauna.

2.5 Fish fauna

Not only the invertebrate fauna is but also the fish fauna changes with the eutrophication. Oligotrophic lakes are often very deep and have cold water, at least in hypolimnion. The fish fauna is thus composed of cold stenotherm species such as Coregonus and Salmo spp. These species are plankton feeders or carnivores.

In eutrophic lakes with warmer water and more vegetation, species of the genera Cyprinus and Leuciscus as well as pike and pike-perch are

dominant. These species are more adapted to warm water and the first two genera mentioned feed on vegetation and small animals living in or on the vegetation belt. They are also more tolerant to a low oxygen content in the water, but even these species can not survive in too low concentrations and can be killed during the winter stagnation period.

2.6 Dysotrophic lakes

These lakes can be characterized in the following way.

They are poor in nutrients and the oxygen concentration in the deep water is in summer and winter zero or near zero, due to the decomposition of floating and settling allocthonous humic material.

The vegetation along the shores is not rich and there is often a Sphagnum belt around the lake. The amount of phytoplankton is mostly small but the zooplankton is fairly rich. The bottom fauna is very scarce because of the unsuitable bottom type and low oxygen concentration.

With the increase of settling allocthonous material, which causes a decreasing depth and an increasing Sphagnum belt the lake will develop into peat bogs, figure 5.

3 FACTORS AFFECTING EVOLUTION

The evolution from the oligotrophic to the eutrophic stage of a lake is influenced by many factors. The main factor is that the lake will be more shallow, and this condition can be reached in different ways. It is very difficult to separate the different factors affecting the development as they are very interconnected. The following list will try to give an idea of how the development can occur.

- 1) The lake will receive allochthonous material which settles on the bottom and diminishes the depth. This can also occur by sedimentation of dead plankton and parts of rooted vegetation (=autochthonous material).
- 2) By erosion the shore line can be broadened and more suitable for rooted vegetation which in its turn reduces the action of the waves on the exposed shore, so that more material can settle in this area.
- 3) The inflow of nutrients from surrounding agricultural areas or with waste water increases the production.
- 4) With diminishing depth the rooted vegetation of emergent plants and also floating-leaved plants can spread further in pace with light reaching the bottom.
- 5) With increasing vegetation the water movement will be reduced and the organic material produced will accumulate on the bottom and the silting up will be enhanced.
- 6) The decreasing water depth will make it possible for grass and herb species and later bush vegetation to invade the fringe area.

The process described above is slow from the beginning but accelerates in the end. Once the lake has reached a high eutrophic level, which can take thousands of years, the development to

arable land can pass in a few decades or hundreds of years.

If the amount of organic material settling on the bottom is very large the lake might develop to a swamp which later will be transformed to a peat bog.

4 PRODUCTION

4.1 Phytoplankton

In connection with the description of phytoplankton it was mentioned that the primary production was low in oligotrophic lakes because of the low concentrations of nutrients. Gessner /4/ has given values from some Danish lakes where the primary production by phytoplankton has been measured by the C-14 method.

| | Tiefe m | Elektrolyt- Gehalt ($\mu\text{S} \cdot 10^6$) | Primärprod. Jahresmittel mg C/m ² /Tag | Compound- Index |
|-----------------------|------------|---|---|--------------------|
| Grane Langsø | 11 | 49— 50 | 260 | 0,3— 0,6 |
| Kattehale Mose | 1,5 | 76— 83 | 80 | 0,7— 0,85 |
| Store Gribsø | 11 | 128—131 | 230 | 4 |
| Furesø | 36 | 290—310 | 770 | 2,3— 4 |
| Frederiksborg Slotssø | 5 | 360—410 | 1320 | 9 —11,7 |

As can be seen lakes with higher conductivity also have a higher production per year.

Ross and Kalff /5/ have measured the production of phytoplankton in a Canadian lake and obtained an annual production of 175-219 g C/m² or an annual average of 480-600 mg C/m² · d. The daily average summer production varied between 794 and 1078 mg C/m² d. The great difference was due to the conditions in different places in the lake.

The daily production in several European lakes has been compiled by Rodhe /6/ who has also shown the correlation between production per m² and per m³. All values (figure 6) are achieved during optimal light conditions and they vary from 20 to >2000 mg C/m² · d.

The production is of course also dependent on the biomass, but not on the number of cells as in the sea where there is a fairly constant relation between net and nannoplankton. In lakes the production is correlated to the weight of the total phytoplankton biomass, figure 7. As an example of a very high production the figures from Lake Trummen in Sweden can be mentioned /7/. Before the lake was restored the production by phytoplankton was $10 \text{ g C/m}^3 \cdot \text{d}$ and was concentrated in the upper 20 cm. The euphotic zone was at that time less than 0.5 m. Only 20-40 % of the production was performed by algae able to pass through a $45 \text{ }\mu\text{m}$ plankton net. The average annual productivity was 375 g C/m^2 before restoration and dropped to 225 g C/m^2 . More than 60 % was however produced by algae less than $10 \text{ }\mu\text{m}$.

4.2 Rooted vegetation

The production of rooted vegetation has not been measured to such an extent as that of phytoplankton and the information is therefore much less. A few examples will however be reported to enable a comparison to be made with the values for phytoplankton.

Schierup /8/ has investigated the total annual net production of Phragmites in a Danish bog and obtained a value of $1760 \text{ g dry weight/m}^2 \cdot \text{a}$ including both aerial parts and rhizomes.

Penfound /9/, quoted in ref 4 reports an American investigation regarding the production of *Typha latifolia* which gave values of 3.84 to $10.94 \text{ g C/m}^2 \cdot \text{d}$. The large variation is due to the values being from different times of the year. The production of floating-leaved and submerged vegetation has

been investigated by Nygard /10/ who has found that a biomass of *Nitella* of 20-40 g dw/m² produced an organic material corresponding to 150-300 mg C/m² · d. In Green Lake, Wisconsin, the production of rooted vegetation is 50 kg d w/har and the phytoplankton has an annual production of 2650 kg/har /11/.

In Mirror Lake, New Hampshire, USA, which is a lake that can be compared with northern European ones, the biomass has been investigated and calculated /12/. The investigator has divided the littoral into three zones. The first 0-2 m has a biomass of about 15 g d w/m². The second one 2-5 m has a much lower biomass, 1.5 g d w/m². The last zone 5-7.2 m shows a higher biomass value which depends on *Nitella* stands that locally exceed 40 g d w/m². For the lake as a whole the hydrophyte biomass is 4.2 g d w/m² or 7.1 g d w/m² if only the colonized zone is used as area. The net production can be estimated to 1.6 g C/m² · y.

4.3 Zooplankton

The production of zooplankton is not so easy to determine and the information is again fairly sparse, but as an example the figures reported by Culver and De Mott /13/ from Lake Eire can be mentioned. They calculated the annual production to be 99.4 g d w/m². In the above mentioned Green Lake the production of zooplankton during a year is 5.3 g d w/m² /11/.

4.4 Bottom fauna

The variation in the biomass of bottom fauna can be very great; it is very dependent on which species are present. In an oligotrophic lake the weight is estimated to be about 1.24 g/m² whereas in a eutrophic lake the weight can be 20-100 g/m².

It is therefore of little interest in this report to give details of the composition and related weights of the bottom fauna in different lakes. However, Table 1 gives an idea of the variations that can exist.

4.5 Fish

Finally the production of fish or the catch for human consumption from different types of lakes could be of interest for possible future work. In figure 8 the fish catch in kg/har · y in relation to the average depth of the lake is given.

As can be seen, the catch decreases rapidly with increasing depth. However, the increased catch is not necessarily so valuable as could be desired since the composition of fish species can change to less valuable ones, as is illustrated in figure 9.

5 PEAT

5.1 The formation of peat

When a lake has reached the state of a bog the bottom is often covered with unfouled plant material. The formation of peat will occur when aerobic microorganisms, bacteria and fungi can decompose the organic material. This process is fairly quick when the material is in the air above the soil. In water the process is slower or impossible due to the low oxygen content. With a high settling rate the organic material will not be decomposed before new material has covered the bottom. With a lower groundwater level or a land uplift the gyttja will be oxygenized and the decomposition by bacteria can start again, which will result in the formation of highly humified peat even in the deeper layers.

The dead plant material contains cellulose, hemicellulose, lignin, wax and resin as well as nitrogenous proteins and amino acids.

Wax and resin are very resistant material and will be unchanged during the peat formation, contrary to the case for cellulose and lignin. The relative concentration of the first two will therefore increase during the process as will also the nitrogenous substances.

The quality of the peat depends therefore on the chemical composition of the peat-forming plants and how far the humification has advanced.

5.2 Types of bogs

Depending on the varying adaptation of the peat-forming plants to different environments, the peats are divided into ombrogene, soligene

and topogene types. The way in which the water is supplied is crucial for the formation.

Ombrogene areas will receive their nutrients and water from precipitation and therefore form a hydrographic unit that is separated from the surroundings.

Soligene areas receive their water supply from the environment and percolation over the surface.

Topogene areas are formed and developed as a result of their location in the environment.

The peat formation in these three main types can occur either by intrusion of higher plants into a lake or by embogging of previously firm soil.

In the south of Sweden the common development has been that a topogene peat area changes to an ombrogene peat bog.

This evolution can be described in the following way.

During Atlantic time a lake was silting up due to evaporation and a high sedimentation rate. At the end of this period a large part of the lake surface was covered by Phragmites and Scirpus. During the following period, the subboreal period, the climate became dryer and a leafy marsh was formed above the overgrown parts of the lake. Gradually towards the end of this period a wood of pine and birch with moss had occupied the leafy marsh and formed a dense forest over the

whole bog. Nowadays a stump horizon in the peat may in many places reveal the existence of this wood.

With the change in climate in subatlantic time the white moss (Sphagnum) invades the leafy marsh. The trees will die and a peat-moss is formed, and Carex-bogs appear in the lagg open water at the edge of a bog.

Most of the bogs in Sweden are a combination of the three main types described above.

6. CONCLUSIONS

The uptake of different elements and also of radioactive nuclides varies with the chemical composition of the water in a recipient. The uptake varies with different species of both plants and animals.

It is therefore important to have a thorough knowledge of conditions such as pH, redox-potential, nutrient contents, composition of flora and fauna in order to be able to calculate how much of an element will be accumulated by plants and animals and how much will be transported to the sediment after decomposition.

The uptake is also dependent on the total production of organic material in the different trophic layers.

As has been reported, the production can vary very much both during the year and in each trophic layer.

In an American lake the production of rooted vegetation was 50 kg dw/har per year and that of phytoplankton 2560 kg dw/har. The fish catch varies from less than 5 kg/har up to 20 kg/har depending on the type of lake.

In order to be able to calculate the amount of an element bound in each trophic layer a knowledge of the production seems necessary.

It can therefore be deemed necessary to study the transport of some elements in the different lake types and also in the peat, and from these studies try to draw conclusions about the behaviour of those radionuclides which might be of interest.

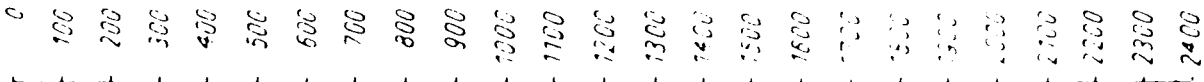
Comparable laboratory studies of the transport mechanisms should also be carried out step by step in experiments where the lake types are simulated.

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Table 1



- 34.7 - Mittel von 2.8 - 240.6 für 16 schwedische Seen (Schlamm)
- 63.5 - Mittel von 0.7 - 324.3 für 18 Finnische Seen
- 59.2 - Mittel von 21.2 - 100.6 für 10 norwegische Seen
- 798.5 - Mittel von 13.1 - 4061.3 für 57 norddeutsche Seen
- 140 - Green Lake in Nordamerika.
- 496.8 - Mendota-See in Nordamerika (Schlamm).
- 287 - die Seen am Illinois. Mittel von 64 - 952
- 744 - Fluß Illinois. Mittel von 12 - 3030
- 477 - Jlmensee Mittel von 285 - 668
- 94.1 - Tschana - See
- 50.6 - Weißer - See
- 10.2 - Schwarzer - See
- 180 - Buseroboje - See
- 933 - Mittel von 241.3 - 1626.2 für das Delta der Wolga bei schwacher Strömung.
- 54.9 - Mittel von 4.4 - 105.2 für das Delta der Wolga
- 2097.6 - (max. 34090.2) schnell fließender Abschnitt der Wolga.
- 139.7 - Mittel von 6.2 - 273.8 für Abschnitte der Wolga mit mäßiger Strömung.
- 75.4 - Mittel von 23.0 - 127.8 für die Überschwemmungsflächen der Wolga
- 1376 - Kaspisches Meer (süßwasserhaltiges Küstengebiet).
- 650 - Brackwassergebiet an der Mündung des Kaspischen Meeres. Mittel von 52.5 - 416.8.
- 28.1 - Kaspisches Meer (Mündungsgebiet mit bedeutendem Salzgehalt).
- 198.8 - Kaspisches Meer. Mittel von 114.1 - 285.5 der Meereszone an der Mündung der Wolga.
- 1600 - Mittel von 200 - 3000 und bis zu 33941.25 der Barents-See. in verschiedenen Biozönosen in der Maschiginer Grube bei Nowaja Semlja.
- 500 - Karisches Meer.
- 270 - Mittel von 50 - 610 des Weißen Meeres in verschiedenen Biozönosen
- 375.8 - Mittel der Ostsee von 0.0 - 1110, in der westl. Ostsee 950 - 1110 in den übrigen Gebieten im Mittel 22.5 - 140 - 172.2, bei Gotland Maximum 612.
- 2670 - Mittel des Asowschen Meeres, in versch. Biozönosen 750 - 910 - 1750 - 3530 - 7450
- 8000 kg Muschelfleisch bei Bewirtschaftung - 37% des Gewichtes mit den Schalen.
- 2238.8 Mittel von 574.6 - 3838.1 für die Küsten Dänemarks bei Limfjord.
- 10425 - Mittel von 32 - 187840 für den Großen Belt im Kattegat.
- 2437 - Mittel von 108.8 - 21254.3 in der Nordsee
- 753.4 - Mittel des südwestlichen Teils der Nordsee in verschiedenen Biozönosen 69 - 251 - 281 - 307 - 981 - 1054 - 2328

Wolga und Kaspisches Meer

} Moskauer Gebiet } UdSSR (s. weiter unten)

Biomasse der wirbellosen Tiere in kg/ha für verschiedene Binnenseen und Meere.

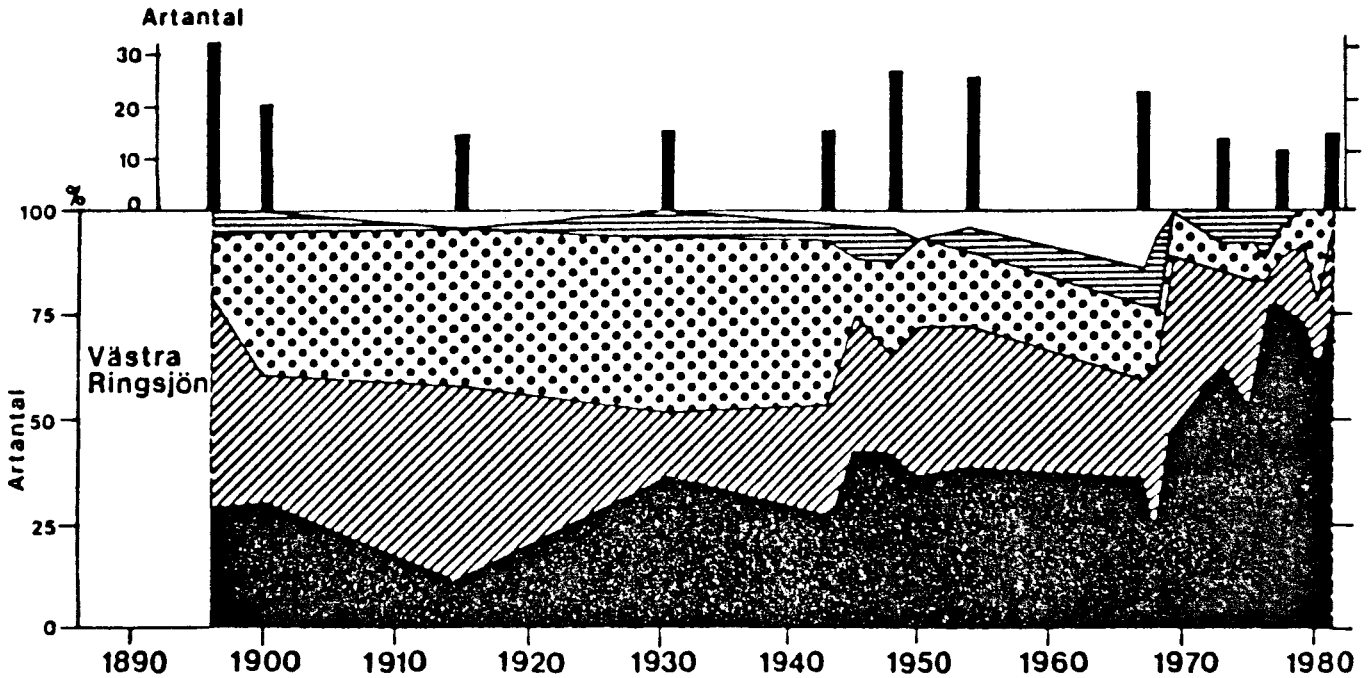
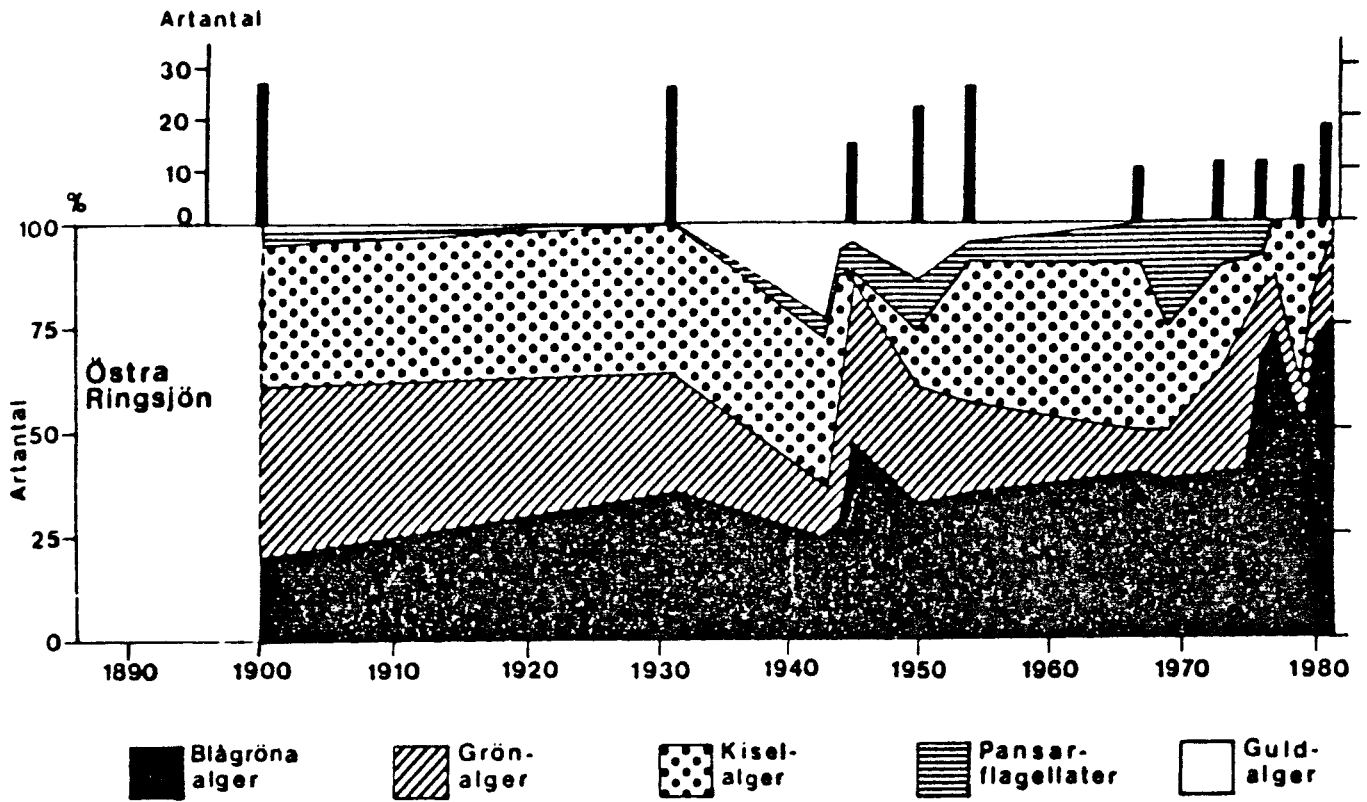


Figure 1. Phytoplankton succession in East and West Ringsjön 1896-198 (IV)

From ref 2

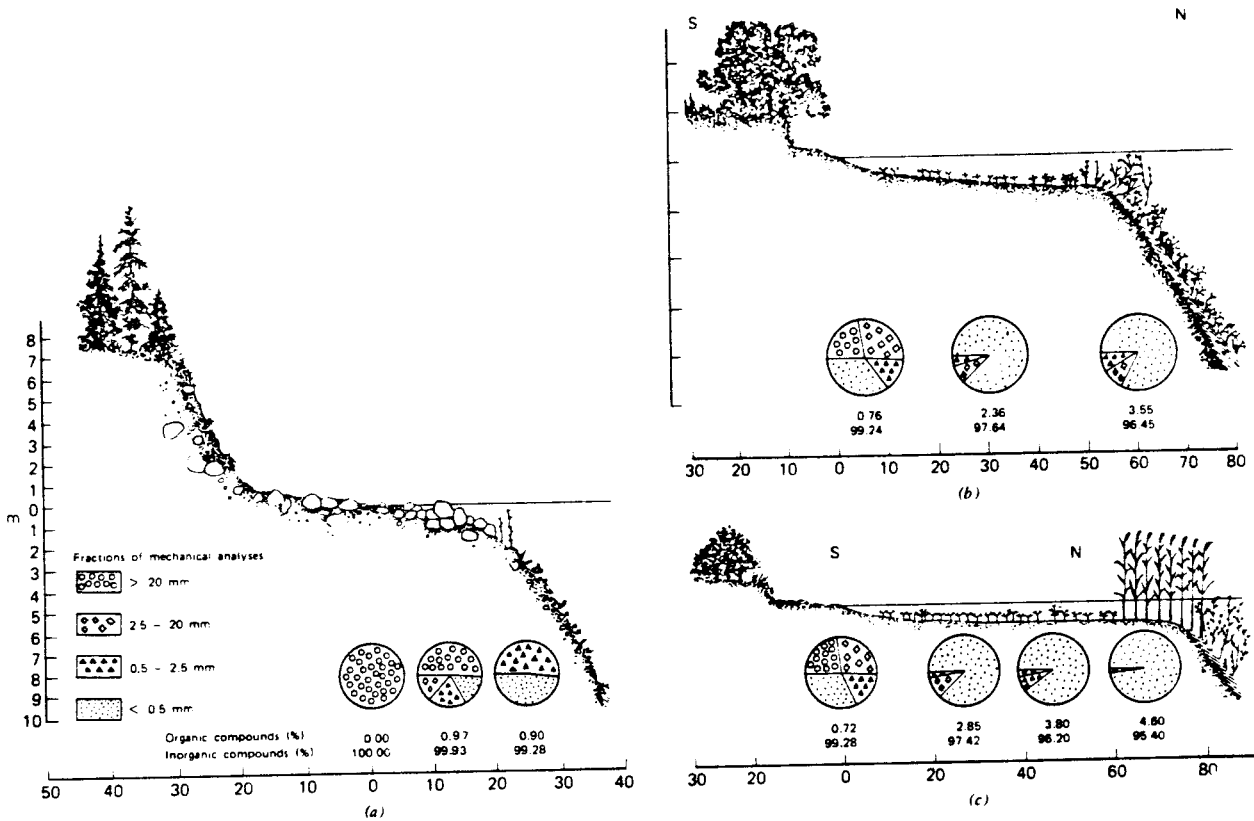


Fig 2. Profile across littoral region of (A) eastern shore of Lake Hańcza, a typical litholittoral; a little *Potamogeton pectinatus* rooted at about 2 m, and below it *Elodea canadensis* to about 9 m. (B) eastern shore of Lake Dargin, a typical psammolittoral; *Parvocharacetum* on sand in up to 1 m of water, *P. pectinatus* and *P. perfoliatus* at top of mont rooted in about 1 m of water, *E. canadensis* and Charophyceae at greater depths. (C) protected southern shore of same lake with psammolittoral bearing a narrow belt of *Phragmites australis* at the lake-ward edge of the shelf, with *P. compressus*, *P. perfoliatus*, *P. lucens*, and *Ranunculus circinatus* rooted in 2-4 m water. Sectored circles refer to the composition of the sediments at the points immediately above their centers (Bernatowicz and Zachwieja).

From ref 2

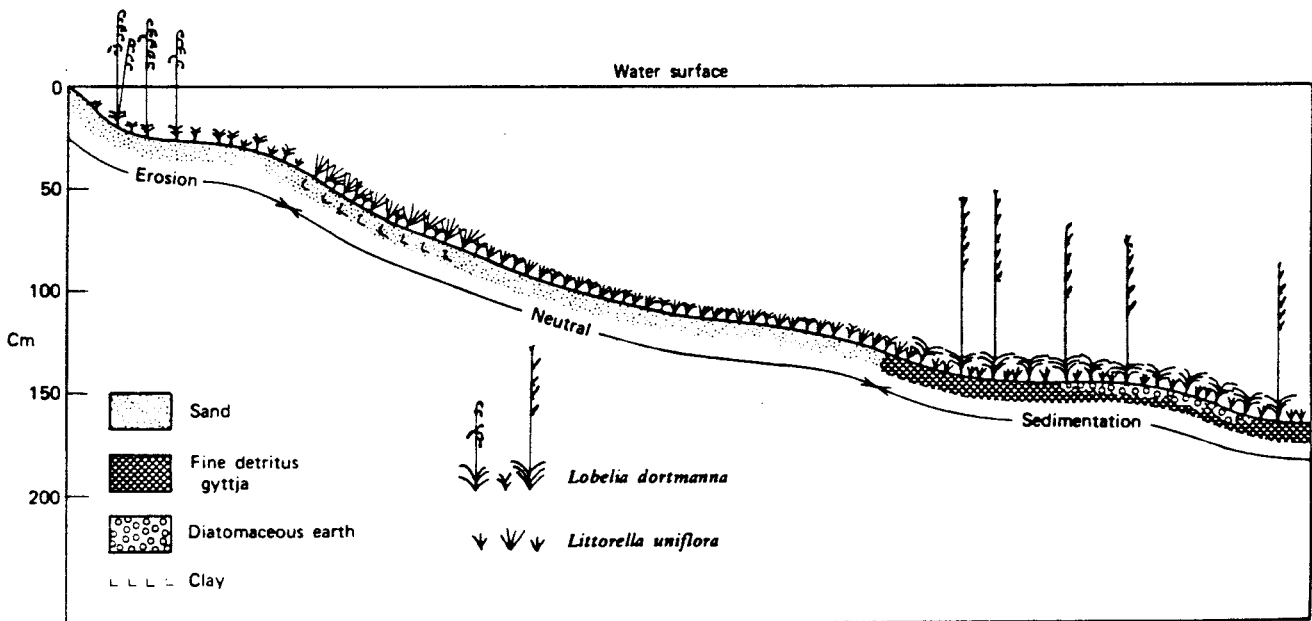


Fig 3. Distribution of *Littorella uniflora* and of *Lobelia dortmannia* on the protected western side of Lake Fiolen. Note the two zones of flowering of *L. dortmannia*.

From ref 2

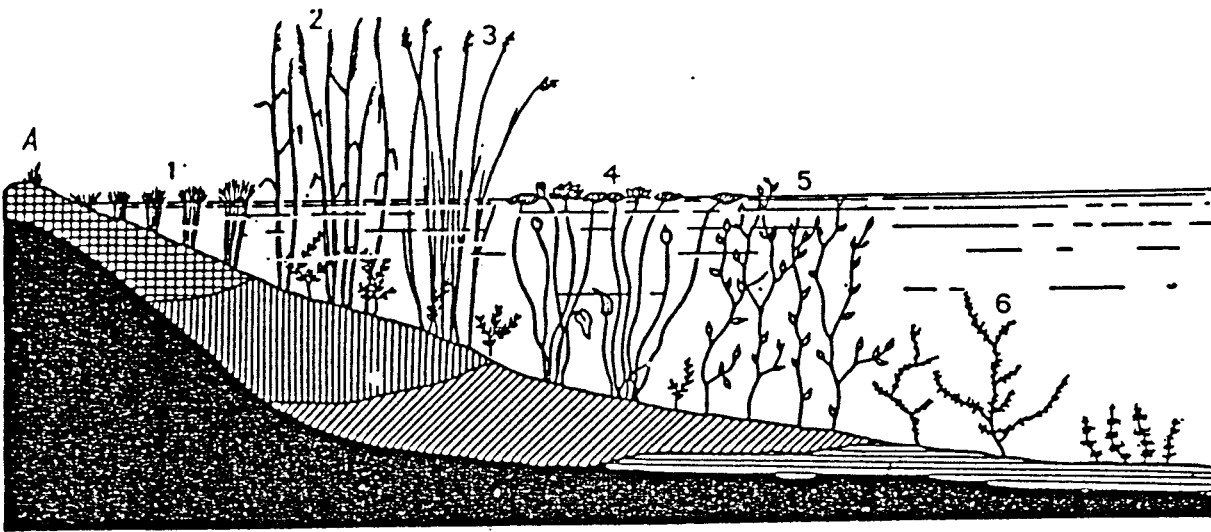


Fig 4. Schema der Verlandung eines Sees.

1 Riedgraszone; 2 Zone des Schilfes, bis zu 2 m Tiefe; 3 Zone des Rohrs, bis zu 3 m Tiefe; 4 Zone der Scerosen, bis zu 4 m; 5 Zone der Laichkrautgewächse, bis zu einer Tiefe von 6 m; 6 Zone der Characeen, bis zu 8 m Tiefe; unter den Riedgräsern (gekreuzt gestrichelt) lagert sich Riedgrastorf ab; unter dem Schilf und dem Rohr findet sich Schilf- und Rohrtorf (vertikal gestrichelt); unter den Zonen der Scerosen und der Laichkrautgewächse liegt Sapropeltorf (schräg gestrichelt); unter der Zone der Characeen Sapropellit (horizontal gestrichelt); schwarz ausgezogen der Boden des Sees.

From ref 11

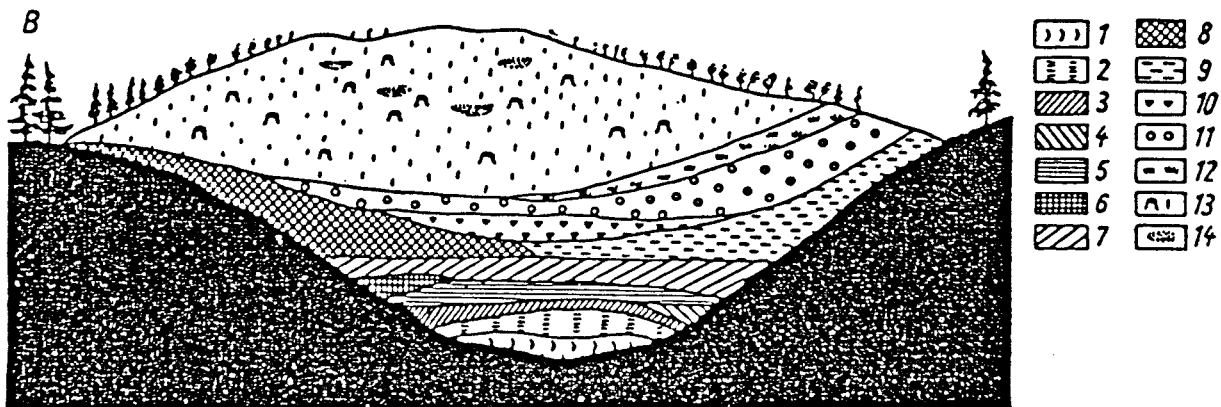


Fig 5. Schema eines Hochmoores, das durch die Verlandung eines Sees entstand.

1 Südwassermergel; 2 Sapropellit; 3 Sapropeltorf; 4 Schilftorf; 5 Rohrtorf; 6 Schachtelhalmstorf; 7 Riedgrastorf; 8 Riedgrasweldentorf; 9 Waldturf; 10 Hypnoturf; 11 Scheuchzeriacentorf; 12 Sphagnumturf; 13 Sphagnumturf mit Fichtenstubben; 14 Wasserlachen auf dem Sphagnumteppich; schwarz ausgezogen der Boden des ursprünglichen Sees.

From ref 11

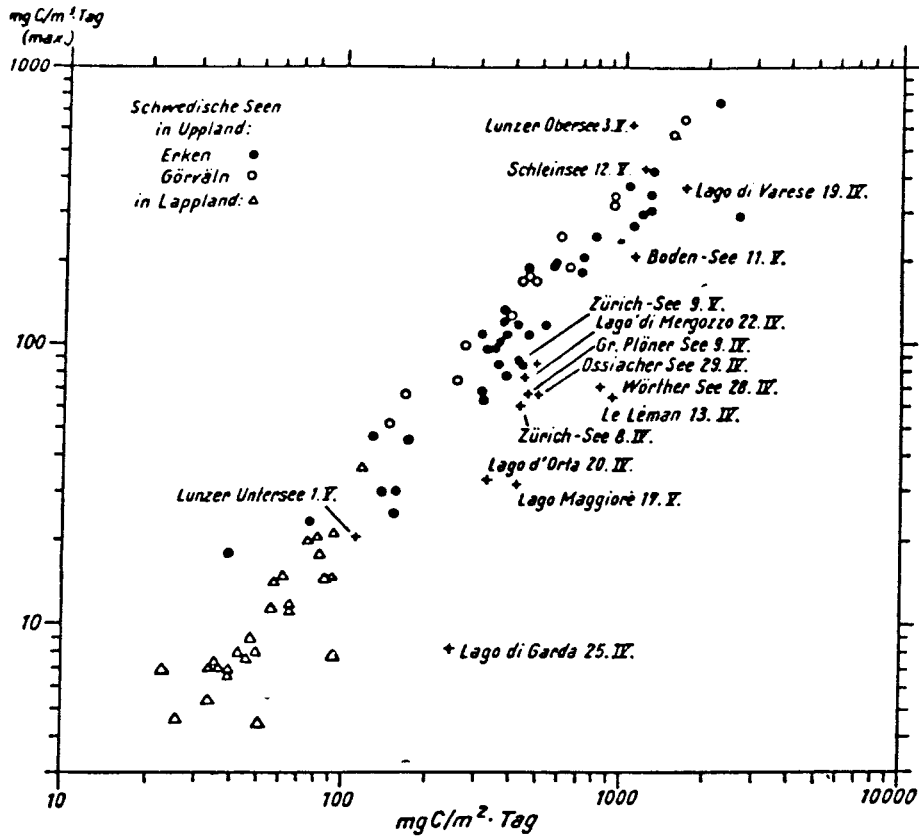


Fig 6. Tagesraten der Primärproduktion in mg C/m^2 in Beziehung zum Volumen maximaler Leistung (mg C/m^3) unter optimalen Lichtbedingungen in verschiedenen Seen Europas, gemessen mit der ^{14}C -Methode in 24 Stunden in situ. (Nach RODHE 1958.)

From ref 6

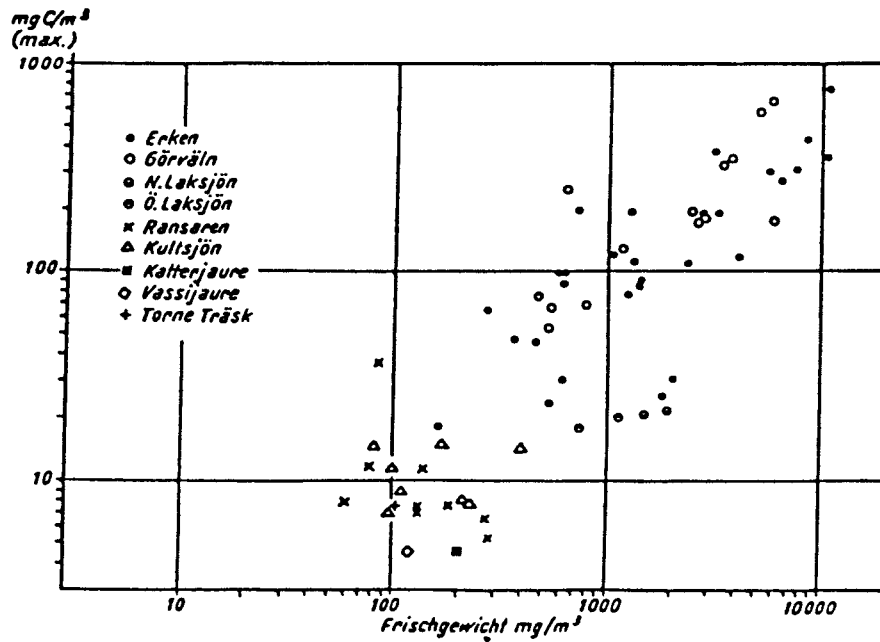


Fig 7. Beziehung zwischen der täglichen Primärproduktion im lichtoptimalen Kubikmeter und der durchschnittlichen Biomasse des Phytoplanktons in der trophogenen Schicht schwedischer Seen. (Nach RODHE 1958.)

From ref 4

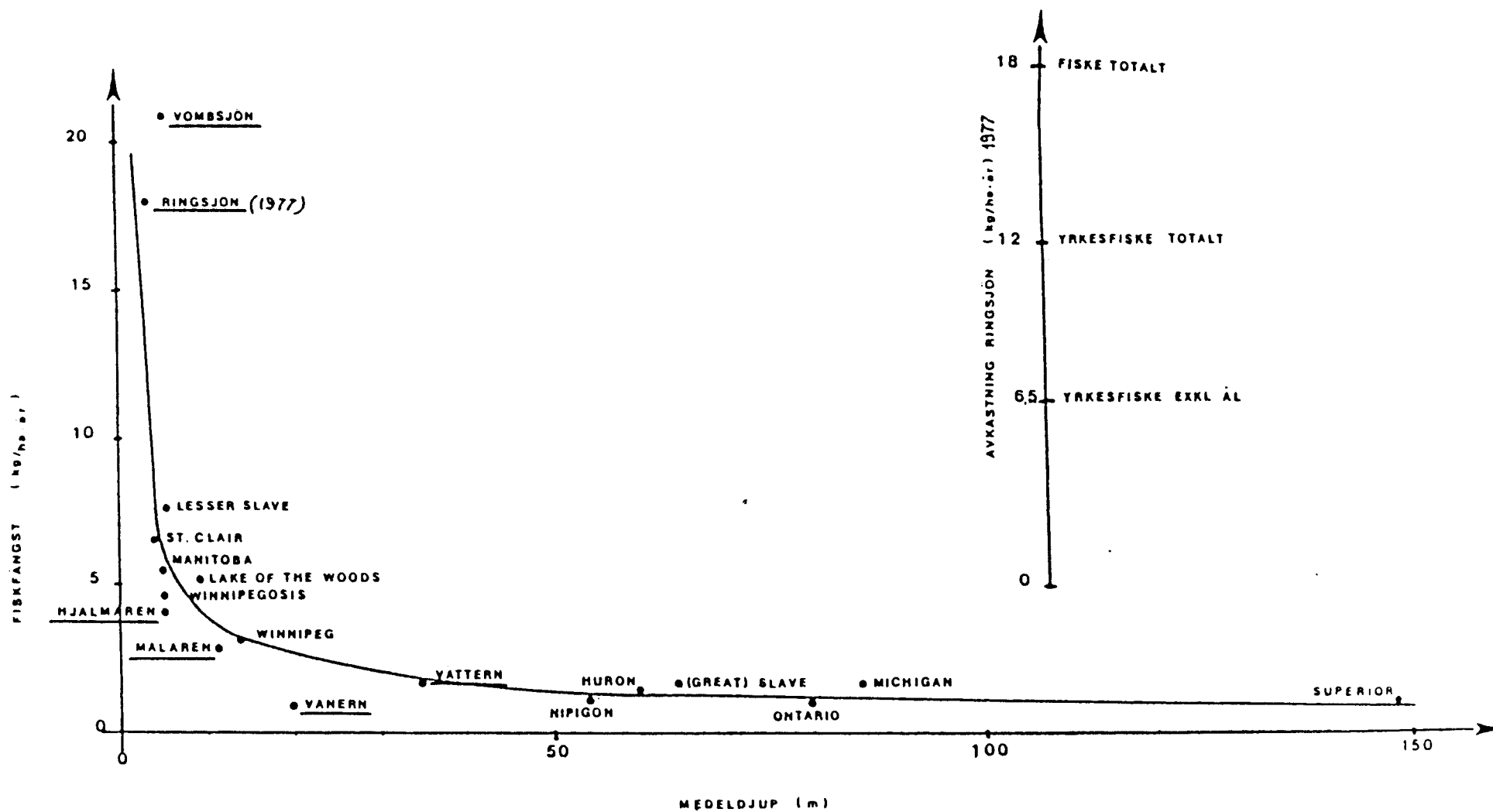


Fig 8. Relation between mean depth and fish production for some lakes (VIII).

From ref 2

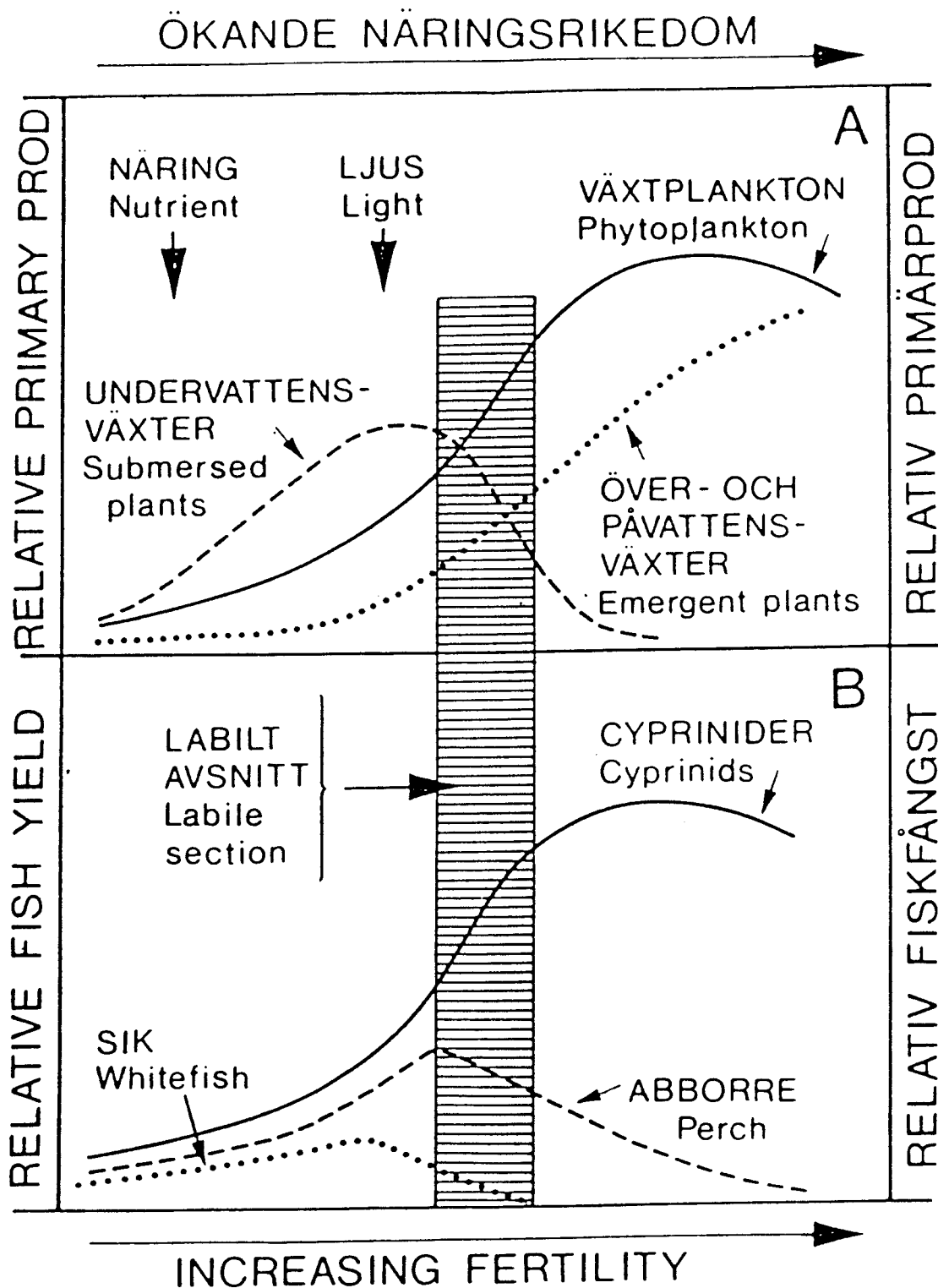


Fig 9. The general relationship between changes in primary production between phytoplankton, submersed plants and emergent plants and the catches of whitefish, perch and cyprinids with increasing nutrient supply in shallow lakes.

1984-08-24

Sverker Evans

ASPECTS OF SEDIMENTATION IN LAKES AND COASTAL
WATERS

ABSTRACT

Because of strong association in general with suspended particles, sediments are normally the major transport vector for pollutants in an aquatic environment. The sediments also act as a sink, effectively removing pollutants from the water column. They may also become a source of pollution long after the releases of pollutants to the recipient have ceased. The structure and composition of a lake or bay sediment is a function of the characteristics of the catchment area and the water column. However, the sediments laid down are also subjected to various short-term perturbations such as resuspension, bioturbation and gas convection. Thus, the uppermost layer of most sediments reflects events occurring near at hand, while the sediments from a defined layer yield information integrated over time. An exceptional case is the formation of varved lake sediments in some Scandinavian lakes which allows calculation of accurate annual deposition values. The major factors governing the distribution of a dissolved constituent in the interstitial water of unconsolidated sediments are diffusion, vertical advection due to sedimentation and compaction, and ion exchange. Furthermore, bioturbation and near bottom currents will induce changes in the pore water composition. Efforts to make long-term forecasts on sediment growth and the subsequent accumulation of elements in the deposits require parameters based on field measurements, and data extrapolated from laboratory experiments.

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1. INTRODUCTION

The whole landscape of the subarctic region is formed by the glacial period and by the tendency of the land mass to rise after being depressed by the ice shield. All lakes in northern Europe have been influenced by glacial activity and the basins are constantly under alteration by exogenous forces such as weathering, erosion, transport and deposition. The sedimentation rate is a function of the surrounding land area from which material is eroded, and the size of the water body in which this material is deposited. Consequently, the sedimentation rate in enclosed or semienclosed water bodies is much higher than the average sedimentation rate in the oceans. The rapid sedimentation and the heavy load of eroded material render these basins, in terms of geological time, shortlived phenomena. Human impingements on lake development such as agricultural activity will furthermore shorten the life-time of lakes and watercourses. It is the ultimate fate of all lakes to be filled up by sediments and in due course be transformed into land.

The role of the sediment is important for several reasons. Because of strong association in general with particles, sediments are normally the major transport vector of pollutants in the aquatic environment. The sediments also act as a sink, effectively removing pollutants from the water column. They may also become a source of pollution long after the releases of pollutants to the recipient have ceased. Thus, the study of sedimentation processes in estuarine and lacustrine environments is of major importance for assessments of the accumulation of elements in various reservoirs, and for long-term risk assessments.

2. LAKE CLASSIFICATION

A scheme where lakes are classified according to their trophic level in relation to the rate of supply of organic matter from allochthonous and autochthonous sources is given in Figure 1. Oligotrophic lakes are characterised by a low primary production and low concentrations of nutrients. Eutrophic lakes in general have a high productivity and high concentrations of phosphorous and nitrogen. Dystrophic or polyhumuos lakes have low productivity and receive a major part of their organic input from surrounding drainage areas. The origin and composition of the sediments in the different lake types may vary accordingly. However, it should be emphasized that in nature there exist only continuous transitions between various lake types.

3. PHYSICAL AND CHEMICAL SEDIMENT PARAMETERS

Sediments, like lakes and estuaries, can be classified according to several principles and by means of numerous parameters. A limited number of physical sediment parameters will be defined. These are: water content, organic content, bulk density and grain size. Most other physical sediment parameters like porosity, permeability and compaction may be defined in terms of these four basic parameters (Håkanson and Jansson, 1983).

3.1 Water content

The water content can be defined as the weight of water related to the total wet weight, i.e.

$$W = \frac{W_w}{W_t} \cdot 100 \quad (\text{Eq 1})$$

where

W = the water content (%)

W_t = the total weight (g)

W_w = the weight of water (g).

The water content of surface sediments varies from about 30 - 50 % in minerogenic deposits to approximately 95 - 99 % in highly organic sediments. The water content is distributed in a typical way in lake sediments. Low values are found in shallow water where coarse material often dominates, while high water contents predominate in deeper parts of the basins. The water content decreases downwards in sediment cores due to compaction.

3.2 Organic content

The loss on ignition is frequently used as a measure of the organic content of lake sediments.

$$IG = \frac{W_s - W_r}{W_s} \cdot 100 \quad (\text{Eq 2})$$

where

IG = loss on ignition in % of the weight of the solid particles (W_s)

W_r = weight of the inorganic residue (g).

3.4 Bulk density

The bulk (= wet) density (ρ) can be determined by the theoretical formula (Axelsson and Håkanson, 1971):

$$\rho = \frac{100 \cdot \rho_m}{100 + (W + IG^o)(\rho_m - 1)} \quad (\text{Eq 3})$$

where

ρ = the bulk density of the sediment
(g cm^{-3})

ρ_m = the density of the solid particles
(g cm^{-3})

IG^o = the loss on ignition expressed in %
of the total wet weight.

This formula is based on the assumption that the density of the water as well as the organic material in the saturated sediment can be set at 1.00 g cm^{-3} . Then the content of inorganic materials (W_s^o) in % of the total wet weight (W_t) can be expressed:

$$W_s^o = 100 - W - IG^o \quad (\text{Eq 4})$$

$$W_s^o = \left(\frac{100}{\rho} - \frac{W}{1} - \frac{IG}{1} \right) \rho_m \quad (\text{Eq 5})$$

The relationship between bulk density (ρ), water content (W), organic content (IG°), and the density of the inorganic particles (ρ_m) is thus theoretically described by Eq 3. Once attached to the sediment bed the mud particles undergo a process of initial consolidation, i.e. a squeezing out of the water between the particles and a gradual increase in density.

3.5 Grain size

In lake sedimentology, the following three grain size classes are the most important (Müller and Förstner, 1968a, b):

sand > 63 μm

silt 2-63 μm

clay < 2 μm

The main grain size is an important tool for the interpretation of sediment data in relation to bottom dynamics. Finer particles dominate in deep waters, where continuous accumulation prevails. In shallow waters, where erosion and transportation dominate, the material is generally coarser. The grain size of the material influences the sedimentation processes and the capacity for entrainment, as well as the capacity of the material to bind pollutants. The potentially active binding area increases significantly with decreasing particle size. (Figure 2).

4. SEDIMENT COMPOSITION

Sediments are formed mainly from material supplied from the terrestrial surroundings of the lake or estuary and from material synthesized in the water column. The sediments contain the following three major components:

- organic matter
- inorganic matter
- inorganic biogenic matter (diatoms frustules and biogenic precipitated calcium carbonate)

4.1 Major and minor constituents

The main groups of elements in lake sediments are summarized in Table 1. Major elements (Si, Al, K, Na, Mg) make up the largest group (80 %) of the sediment matrix in most Nordic environments. Carbonate elements (Ca, Mg and CO₃-C), nutrient elements (org C, N, P) and mobile elements (Mn, Fe, S) make up approximately 20 % of the sediments. The smallest group, the trace elements (Hg, Cd, Pb, Zn, Cu, Cr, Ni etc) constitute less than 0.1 % of the sediments (Kemp et al, 1976).

4.2 Organic compounds

Organic matter represents all types of biogenic particulate matter in various stages of decomposition. The particulate matter form a substratum for bacteria, protozoans, diatoms and fungi. This living microcosmos forms the diet of the detritus feeders, while the non-living component is discharged as fecal pellets, only to undergo further decomposition through repopulation with bacteria. Organic matter which survives degradation in the water column is incorporated in the sediments

where it can be more or less preserved or subjected to further biological degradation. High IG values in sediments are favoured by the following three factors (Håkanson and Jansson, 1983):

- anthropogenic discharges of organic material
- high productivity
- reduced conditions in the sediments which hamper degradation of organic material

The low molecular end products of the decomposition processes in anaerobic sediments such as H_2S , CH_4 and NH_3 migrate upwards and, reaching the aerobic top layer of the sediment, they are oxidized by aerobic bacteria, mostly chemoautotrophes. The organic content is highly correlated to the water content and hence is distributed in sediments in much the same way (Figure 3). The relationship between the bulk density (ρ), water content (W), and organic content (IG°) is viewed in Figure 4.

4.3 Humic compounds

Humic matter is formed mainly as a result of the degradation of plants and can be of allochthonous as well as autochthonous origin. Humic compounds constitute a dominating part of the total organic carbon in many sediments and are most important for the metabolism and turnover of many inorganic elements, particularly metals and phosphorous. The most important compounds used for the synthesis of humus are lignin, carbohydrates, proteins and phenolic compounds. Further degradation gives humic acids, fulvic acids and a number of gaseous respiration products. Humic compounds are broken down

very slowly. Of the functional groups in humus, carboxyl and phenol groups are of particular interest. They react with positive ions, giving humic compounds ion-exchange and metal-complexing capacity. The ability to bind metals is essential, since humic-rich sediments can thereby neutralize the toxic effects of heavy metals. Humic materials affect the pH of lake sediments and may serve as a buffer.

5. EXCHANGE BETWEEN WATER AND SEDIMENT

Part of the water within the sediment layer is bound in chemical structures or is tightly adsorbed to the sediment particles. The rest constitutes the mobile medium which takes part in exchange processes between the solid and dissolved phases. The interstitial water serves as a carrier of elements between the sediments and the overlaying water and its existence assures continuity of the aqueous phase over long sections of the sediment layer. This will enable chemical species to migrate within the sediment as well as across the sediment-water interface.

The major factors governing the distribution of a dissolved constituent in the interstitial water of unconsolidated sediments are diffusion, vertical advection due to sedimentation and compaction, and ion exchange. Furthermore, bioturbation and near bottom currents will induce changes in the pore water composition. Of the several mechanisms responsible for the movement of materials across the sediment-water interface, ordinary diffusion is probably the least important. Mixing of the sediment by the burrowing activity of deposit-feeders is far more important and may result in homogenization of the chemical composition of the upper sediment layer. An important control on pore water chemistry also occurs when infaunal organisms pump overlaying water through their burrows in order to replenish their oxygen or food supplies. A "biological pumping rate" of water across the interface of $0.7 \pm 0.3 \text{ cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$ was calculated by Luedtke and Bender (1979) for the sediment of Narragansett Bay (USA).

6. DYNAMICS AT THE BOTTOM BOUNDARY LAYER

The structure and composition of a given lake or shallow bay sediment is a function of the characteristics of the catchment area and the water column. However, the sediments laid down are also subjected to various short-term perturbations such as resuspension, bioturbation and gas convection (Figure 5). Thus, the uppermost layer of most sediments reflects events occurring near at hand, while the sediments from a defined layer yield information integrated over time. The resolution in time is generally governed by the sedimentation rate. However, the sedimentation within a basin may also vary considerably. This implies that a selected sediment layer may represent a different time-span even when sediment cores are collected in close proximity to each other. Consequently, most sediments only provide a long-term average of the trophic level of a basin.

6.1 Sediment transport

Physical disruption of the sediments may result in resuspension of sediment particles. Once in suspension, a load of sediment can be transported a considerable distance before settling to the bottom. A number of empirical experiments have been made to determine the critical flow-velocity needed to start a particle into motion. As one might expect, the critical fluid-flow increases with grain size. An exception to this rule is noted for cohesive clay bottoms. Because of their resistance to friction they need rather high velocities to erode them (Figure 6). On the other hand, biological activity can destabilize the sediment by the destruction of sediment cohesion through burrowing (Yingst and Rhoads, 1978). This will increase the roughness of the surface layer sufficiently to enable particles of sediment to be picked up by weak bottom currents not capable of

erosion on their own (e.g. Evans, 1982). MacIlvaine and Ross (1979) have emphasized the importance of biota in determining surface roughness and sediment erodibility. Fecal pellets also seem to be more easily eroded compared to the ambient sediment (Rhoads and Young, 1970). However, benthic infaunal organisms may also stabilize the sediment by producing mucous coatings on the walls of their burrows. Woodin (1976) found that dense tube mats could cause an increased resistance to erosion.

6.2 Sedimentation rates

The sedimentation rates of three eutrophic lakes in Sweden were calculated by Edberg (1980) using ^{137}Cs fallout data (Table 2). The deposition in lake Ekoln was 2800-3400 g m⁻² dry wt (Håkanson, 1976).

El-Daoushy and Johansson (1983) reported some sedimentation data from Swedish woodland lakes. These lakes were situated on bedrock which was covered with thin layers of moraine, and had low primary production because of lack of nutrients. The sedimentation rates were accordingly low and varied from 0.5 to 1.2 mm yr⁻¹. The accumulated amounts m⁻² of sediments, integrated over 25 year intervals, and the totals which represent integrals for 125 years, are presented in Table 3.

Generally, the deposition rate increases in a linear fashion with increasing water depth. In open water areas the maximal values are found in the deepest parts of the basin. In small lakes where the deposition pattern is fairly unaffected by external factors such as wind stress and waves, high correlation is found between the rate of deposition and the water depth (Figure 7, top). In large lakes, on the other hand, the deposition is highly influenced by hydrographical factors and

the correlation is significantly less between deposition rate and water depth (Figure 7, bottom).

6.3 Bioturbation

Bioturbation can be defined as the added effect on the mobility of elements from bacterial activity, microbiological gas convection, burrowing benthic organisms and from fishes hunting prey items on or within the sediment. Bioturbation plays a significant role in modifying the sediment properties by

- altering the distribution and the size of the sediment particles
- changing the bulk characteristics of the sediment such as its permeability
- varying the boundary properties of the near-bottom flow by altering the roughness of the sediment bed.

The depth range of bioturbation generally comprises the upper 5 - 10 cm of the bottom substrate. Most of the bioturbation that occurs near the sediment-water interface is performed by deposit-feeding invertebrates which rework the sediment they ingest. Several experimental investigations concerning flux rates of nutrients, heavy metals and radioactive trace elements in sediments have given evidence of the importance of bioactivity for the release of elements to the water column. Holdren and Armstrong (1980) investigated factors affecting the release of phosphorous from intact sediment cores. Bioturbation was found to have the greatest effect on phosphorous release by changing the chemical conditions of the pore water, while sediment suspension removed phosphorous from the water column. Boddington et al (1979) recorded a significant density-dependent loss of mercury from sediments holding tubificid worms. The loss occurred mainly from the uppermost cm of the sediment. Renfro

(1973) performed experiments to determine the loss rate of ^{65}Zn from a marine silty sediment. 3 - 9 % of the absorbed zinc was desorbed within 30 days. The burrowing activity of polychaete worms caused losses 3 - 7 times higher through resuspension of fine particles and, possibly, due to loss of dissolved zinc. Rates of biogenic reworking by different benthic invertebrates are viewed in Table 4.

The effects of bioturbation on the mobility of elements decrease downwards in the sediment due to a reduced population density and an increased sediment compaction. However, to appraise the stratigraphic importance of bioturbation, we must also know the sedimentation rate. The impact of bioturbation is greater if the sedimentation rate is low, because deposits from more years are involved in the mixing process.

6.4 Formation of varved lake sediments

In Scandinavia and certain parts of North America, varved lake sediments seem to occur quite commonly. In northern Sweden, 14 lakes in which the entire sediment deposit is varved are at present known (Renberg, 1982). The longest sequence so far found comprises almost 9 000 varves. In consolidated sediments from northern Sweden, varve thicknesses of 0.1 - 1 mm have been recorded. In unconsolidated sediments the varve thicknesses is greater, usually between 1 - 4 mm, but occasionally up to 10 mm (Renberg, 1982). The basic conditions for the formation of varved lake sediments are the seasonal variations of the climate, which produce an annual rhythm in the sedimentation of both biotic and abiotic materials. However, varve formation is realised only under certain pre-conditions. The sediment should remain undisturbed once it has been deposited on the bottom and not become mixed

due to bioturbation, water movements, gas convection or other causes. Bioturbation is the most deleterious factor with regard to varve formation.

In Sweden, all lakes in which varved sediments are known are dimictic, i.e. they circulate twice a year, generally in spring and autumn. In thermally stratified lakes with a high productivity or a substantial influx of allochthonous organic matter anaerobic conditions arise in the hypolimnion during the summer and/or winter months. This leads to a seasonal depletion of the benthic fauna, and the probability for an undisturbed sediment growth will increase.

The quality of the varves is best in the deepest parts where the stagnant conditions will prevail longest. Mechanical disruption of the surface sediment due to water movement appears to be relatively slight. Conditions for varve formation are further improved when the lake bottom is flat which ensures minimal physical disturbance of the deposited sediment.

The seasonal sedimentary succession is well reflected in the annual layers. First, a layer of mineral grains is visible which has been deposited during the snow-melt period. Above follows a layer of predominantly biological material such as algal remains and pollen which is deposited during the summer period. Above this layer is a thin layer composed of organic material deposited beneath the ice-cover of the lake (Renberg, 1982).

6.4.1 Sampling of varved sediments

The surface sediment of a lake is often very loose and sampling is usually a difficult operation. However, the crust-freeze method yields undisturbed

samples and is the best method to use when samples of the unconsolidated surface sediment are to be obtained for varve-counting and analysis (e.g. Saarnisto, 1979; Renberg, 1981).

6.4.2 Varve-counting and dating

The individual levels in a varved sediment can be dated by making varve-counts, and accurate annual deposition values can then be calculated. The error of the dates given by the varve-counts normally does not exceed ± 2 % (Renberg and Segerström, 1981). An exact geochronological dating method for events during the Holocene period is particularly valuable, considering the problems which can be encountered in connection with the radiometric dating of sediment samples. Up to the present, various radiometric methods have been used in stratigraphic investigations. However, during the past few years, the reliability of the dates obtained primarily by the ^{14}C method has been more often brought into question; dating using this method sometimes makes the dates several hundred years too high or too low (Renberg and Segerström, 1981).

Compared with normal homogeneous lake sediments, annually laminated lake sediments have many advantages. Samples of known age can be analysed and e.g. pollutant influxes can be determined with a high resolution in time. The absolute dates obtained by varve-counting also help to estimate other time-related events such as the land uplift. A new shore-line displacement curve for southern Västerbotten province has been obtained by dating varve counts of sediment cores from lakes situated at different altitudes above the present sea-level (Renberg and Segerström, 1980).

7. ESTUARIES AND BAYS

An estuary is by definition a region containing a volume of water of mixed origin derived partly from a discharging river system and partly from the adjacent sea, the region being partially enclosed by a land mass (Barnes, 1974). A coastal bay is a body of water semi-isolated from the sea by a ridge etc. Fundamentally, estuaries and bays differ in the width of their connections with the sea and, thus, in the rate of fresh-water inflow. Bays tend towards comparatively small fresh-water inputs. Their salinities are generally more stable than those of estuaries.

The geomorphological character of estuaries has a pronounced influence in determining the nature of the processes operating within any given estuary. Because one end of an estuary grades into fresh water and the other is open to the sea, it follows that a salinity gradient of some form will exist along the estuary. The dominant salinity regimes vary from a state of little mixing between the fresh and salt water masses (salt-wedge estuaries) to more or less complete mixing due to current-induced turbulence in areas with strong tidal influence.

7.1 Deposition in estuaries

The mixing of fresh and salt waters has considerable effects on the deposition of particulate matter in the estuary. By the time most rivers reach the sea, they have already deposited the coarser sediments in their upper reaches. Silt particles, however, are transported in suspension in the lower reaches of most rivers and will be discharged into the adjacent estuaries. On contact with a medium containing high concentrations of

cations, these silt particles tend to flocculate, so that at the zone where fresh water meets water of high ionic strength, the silt particles clump together and sink more rapidly. Observations on different flocculation of suspended particles of colloidal or semicolloidal dimensions are restricted to clay minerals (Whitehouse et al, 1960). The most common clay mineral types are kaolinite, illite, and montmorillonite. Less common clay types are vermiculite and chlorite; the latter mineral is frequently found in marine sediments. It has been found that clay mineral particles usually have a negative charge, which may be explained by preferential adsorption of anions, especially hydroxyl ions, and cationic substitutions within the crystal lattice (Postma, 1967). Because of structural differences, different types of clay minerals flocculate in different manners. Experiments have shown that flocculation of kaolinites and illites occurs in salinities of less than 4 o/oo, whereas the flocculation of montmorillonite increases gradually with increasing salinity and thus continues over the whole estuarine salinity range (Barnes, 1974). In rapidly moving water the various clay minerals may be transported without differentiating, but at low current velocities illites and kaolinites may be deposited, whereas montmorillonites remain in suspension. The difference may be greater in fresh and brackish water than in ocean water.

In most semi-enclosed water bodies, net deposition exceeds erosion so that there is an overall accumulation of mud. In those estuaries in which sea water is the dominant water mass, the bulk of the deposited material is of marine origin. Under the comparatively sheltered conditions prevailing close inshore, the mud may settle out. This process is

greatly accelerated by the presence of salt-marsh vegetaton. Thus, through the dual action of shelter and flocculation, estuaries and lagoons tend to be regions in which fine sediments are trapped.

A discussion of coastal features must inevitably contain a consideration of the recent history of coastal development. According to prevailing opinion, a rapid rise in sea level from about 100 m below the present level started around 17 000 years A D and reached a level 3 - 5 m below the present about 6 000 years A D. Thereafter the sea rose slowly to its present level which was reached about 2 000 years ago (Gorsline, 1967). Gorsline also suggested that the present coastal configurations have been moulded predominantly by processes operating only over the past 6 000 years and in many cases less than 3 000 years.

There are several estimates of sedimentation rates for various marginal marine environments. In humid regions with major river sources, the rate of accumulation can be very high, such as in the delta of the Mississippi, where a maximum value of 300 m/1 000 yr was estimated by Shepard (1960). In bays and estuaries an accumulation of 2 - 4 m/1 000 yr may occur (Shepard, 1953). In arid regions, the rate of accumulation may be very low because sediment can be supplied only by winds and the sea. Rusnak (1960) reported an accumulation rate of only 1 m/1 000 yr. However, neglecting the extremely high sedimentation rates represented by the deltas, the rate of accumulation for the marginal marine environment is about 2 m/1 000 yr for humid bays and estuaries, and 1 m/1 000 yr for arid and semi-arid lagoons. These rates apply only to the accumulation which has occurred since the post-glacial rise of sea-level. An upper limit of sediment accumulation

based on the overall time-average rise in sea level would have to be not greater than 6 m/1 000 yr over the span of the last 15 000 years (Rusnak, 1967).

In terms of the earth's geological history, individual estuaries are relatively transient phenomena. Assuming a constant sea-level in the future, many existing estuaries will be filled by deposits and be extinct. As sediment accumulates, it is invaded by salt-marsh vegetation and will become stabilized. The deposition rate is accelerated and a bar may be formed across the mouth of the estuary, which can exclude the inflow of sea water. The resulting enclosed water body will rapidly develop into a swamp or into marshland and finally into the climax vegetation typical of its geographical region. Conversely, erosion may widen the mouth of an estuary, so that it will gradually become a shallow coastal bay. If the barrier separating a water body from the influx of sea water becomes complete, contact with the sea is usually only via seepage through the barrier and such bays quickly become fresh. All semi-enclosed water bodies are ephemeral, either reverting to the sea on destruction of the barrier, or evolving through marsh stages into land. The silt and detritus frequent in estuaries and shallow bays make such areas extremely fertile and the land so formed may be used for agricultural purposes.

7.2 Sedimentation rates in the Baltic Sea

With the retreating continental ice sheet, the sea floor of the Baltic became covered by erosional material which formed a more or less uniform layer of stratified sediments. Further, a substantial part of the sea bottom consists of postglacial clays and muds covering the older sediments. The

term postglacial is used to denote the sediments occurring above the *Litorina*/*Ancylus* boundary (Winterhalter, 1972). The mean thickness of the postglacial sediments in the Bothnian Sea is about 1.9 m, which gives an annual sedimentation rate of 0.3 mm (Winterhalter, 1972). In the central part of the Gotland Deep, the maximum total thickness of the *Litorina* and post-*Litorina* sediments amounts to 7 m. Considering a duration of 7 000 years from the *Litorina* era to present-day conditions, this would imply a yearly sedimentation rate of 1 mm (Ignatius et al, 1971). By means of ^{210}Pb measurements, an annual sedimentation rate of 1.0 - 1.3 mm was calculated. This suggests that the deposition rate has been very uniform for several thousand years. The results from the Baltic Proper show that the deposition rate hardly exceeds 1 - 2 mm yr⁻¹. This is in good agreement with the values 0.1 - 2.0 mm yr⁻¹ given by Ignatius (1958) for the average sedimentation rate in the Baltic. The sedimentation rate in the West Bornholm Basin varies in its different parts; an average value of 0.5 - 1.5 mm yr⁻¹ is given by Kögler and Larsen (1979).

The amount of suspended matter in the southern Baltic is estimated to be $432 \pm 72 \text{ mg m}^{-3}$ dry wt during winter and $993 \pm 382 \text{ mg m}^{-3}$ during summer (Lenz, 1974). 80 % of the particulate matter ranges between 1 - 150 μm . Organic detritus contributes to the main fraction, followed by phyto- and zooplankton. In the southern part of the Baltic about 500 g m^{-2} dry wt is deposited annually, corresponding to a sedimentation rate of 2.5 mm yr⁻¹ (Zeitschel, 1965).

8. MODELLING OF SEDIMENTARY PROCESSES

Efforts have been made earlier to model the physical parameters of recent sedimentary deposits (e.g. Håkanson, 1977), the effects of bioturbation (e.g. Håkanson and Källström, 1978), and the migration of trace elements in lake sediments (e.g. Lerman and Lietzke, 1975; Booth, 1975; Vanderploeg et al, 1975).

Before developing a model, the following points must be carefully considered:

- A precise definition of the objectives of the model.
- Identification of critical processes (e.g. hydraulic characteristics, sediment characteristics) that must be included in the model.
- Suitable approximations that must be made according to the relative importance of the different processes.
- Field monitoring and experimental work in the laboratory designed to give relevant measurements of the model parameters.
- Sensitivity analysis of critical steps in the model.

The objectives of the model must be to gain a better understanding of the different processes occurring in the natural systems and to provide a tool for decision making. The field and laboratory work must be planned and executed bearing in mind that all relevant physical, chemical and biological processes must be identified. The sensitivity of the model must be examined. The model result will be more sensitive to the value of some parameters than others. These parameters must be more accurately defined, presumably by a more intensive sampling effort or laboratory work.

Generally, the aim of a sedimentary model should be to describe how physical and biological parameters interact in recent deposits in areas where material is being deposited. The model should also enable the calculation of upward and downward transportation of material and determination of the vertical distribution of elements deposited during defined periods of time. Critical data in the model are recipient data (morphometrical shape, residence time of the water), sediment data (sedimentation rate, chemical and physical sediment parameters such as porosity, K_d etc) and biological data (uptake in benthic invertebrates, bioturbation rate etc).

9. CONCLUSIONS AND RESEARCH PROPOSALS

Theoretical models of ecological processes in estuarine and lacustrine environments call for data suited to the calculation of sediment budgets in relation to space and time. Accurate long-term forecasts about sediment growth and the subsequent accumulation of elements in the deposits laid down require a knowledge of production rates and sources of particulate matter, sedimentation rates, affinity of elements to solids, mobility of elements when deposited on the sediment bed etc. Efforts to model sediment dynamics must be based on parameters derived from field measurements together with data extrapolated from laboratory experiments.

The following parameters should be given priority:

- Determination of the sediment growth.
- Determination of basic sediment parameters.
- Determination of the forcing functions of radionuclide migration within the sediment bed.

The parameter of main interest is the sediment growth. However, the sedimentation rate is far from uniform, either in space or in time. Consequently, the sediments from a defined layer only provide information that is integrated over longer periods. The resolution in time is highly governed by the sedimentation rate which varies from about $50 \text{ g m}^{-2} \text{ yr}^{-1}$ in oligotrophic waters to about $3\ 000 \text{ g m}^{-2} \text{ yr}^{-1}$ in eutrophic waters. Thus, the measurement of the seasonal sedimentation rate is of crucial importance for the interpretation of sediment growth within a water body. The sediment growth in Sibbofjärden and Trobbofjärden

should be determined using sediment traps and the variations in the sedimentation rate both within and between years should be established during a two-year period.

The interstitial water within the sediment layer serves as a carrier of elements between the sediments and the overlying water. This will enable chemical species to migrate within the sediment as well as across the sediment-water interface. In order to classify the physical environment in which the radionuclides are resident, it will generally be enough to determine a limited number of sediment parameters: water content, organic content, bulk density and grain size. Most other physical parameters such as porosity, permeability and compaction may be defined in terms of these basic parameters.

The sediments are subjected to various short-term perturbations such as seasonal variations in the sedimentation rate, resuspension by near bottom currents and bioturbation due to the micro- and macrobiological activity occurring within the deposits. These physical and biological factors will to a large extent govern the chemical status of the sediment bed. The mobility of radionuclides within the sediment will vary accordingly. In order to identify critical processes, experimental work should be performed in the laboratory and in the field. Radionuclides should be implanted in sediment cores and the propagation of elements within the sediment then correlated with environmental and sedimentary characteristics. In order to obtain "real world" conditions, a set of cores with implanted activity will also be restored to the Sibbofjärden and Trobbofjärden areas. At regular intervals of time, a number of cores will be

analysed with respect to physical and chemical characteristics and radionuclide contents. As long-term measurements are desirable, the implantation tests should also be performed over a two-year period.

The field and laboratory work should be planned and executed with the objective of developing a sedimentary model. This model may predict the transportation of radionuclides deposited in the sediments. In the laboratory, the effects of critical parameters on radionuclide mobility will be studied. A mathematical model of a laboratory experiment has two aims: to reveal the interactions and causal relationships between its variables, and to make predictions about the behaviour of the system under study. Since it is not possible to model all the complex interactions, the first stage in building a model is to formulate a simplified expression of the system. The next steps are to estimate and select the parameters of this simplified expression. The final step is to compare the data generated by the mathematical model with the experimental data obtained.

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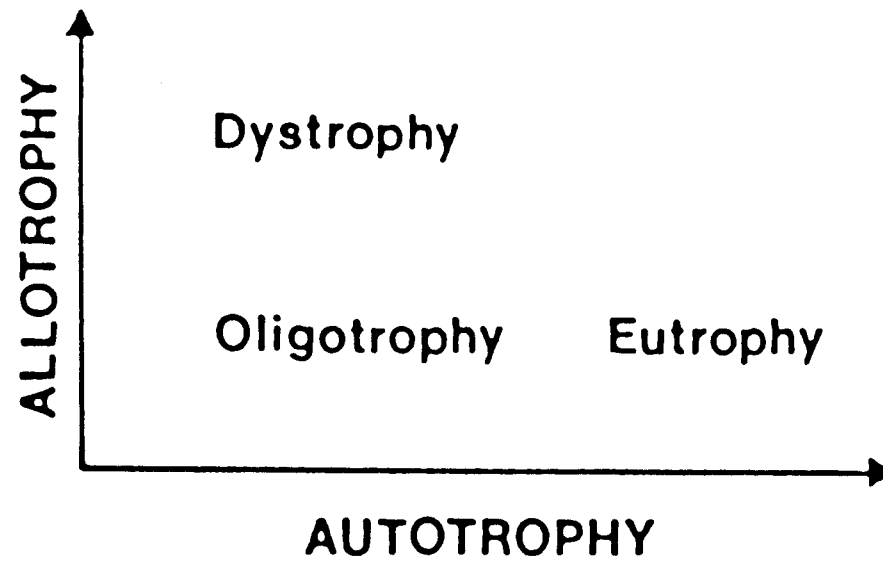


Figure 1

Trophic types of lakes; from the relationship between the supply of organic matter from autotrophic (inside) and allotrophic (outside) sources (Wetzel 1975, Rodhe 1969)

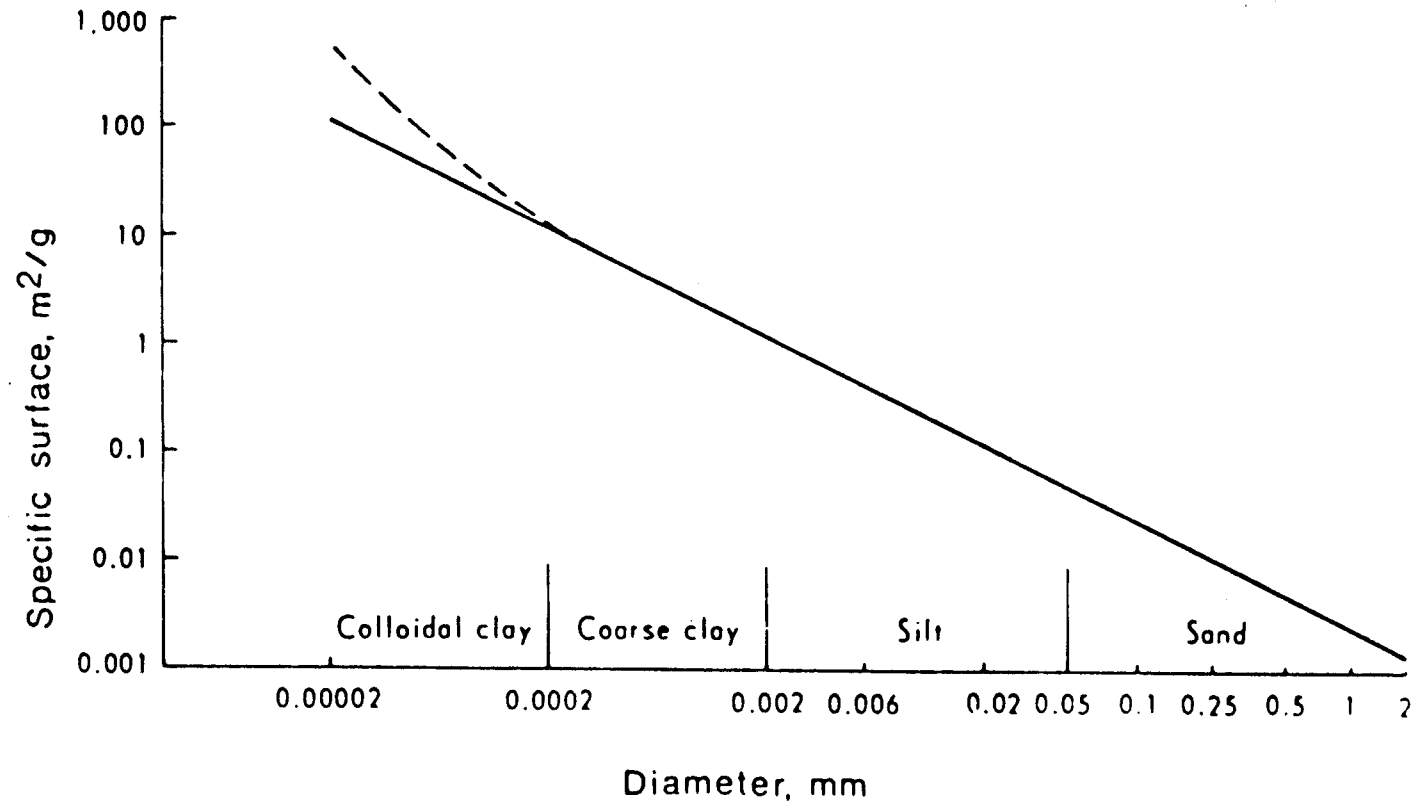


Figure 2

Relationship between particle size and approximate specific surface. Full line is calculated for spheres of density 2.65 g/cm³. Broken line accounts for the fact that clay particles are more plate-shaped and that fine clays have a large internal surface (Kohnke 1968)

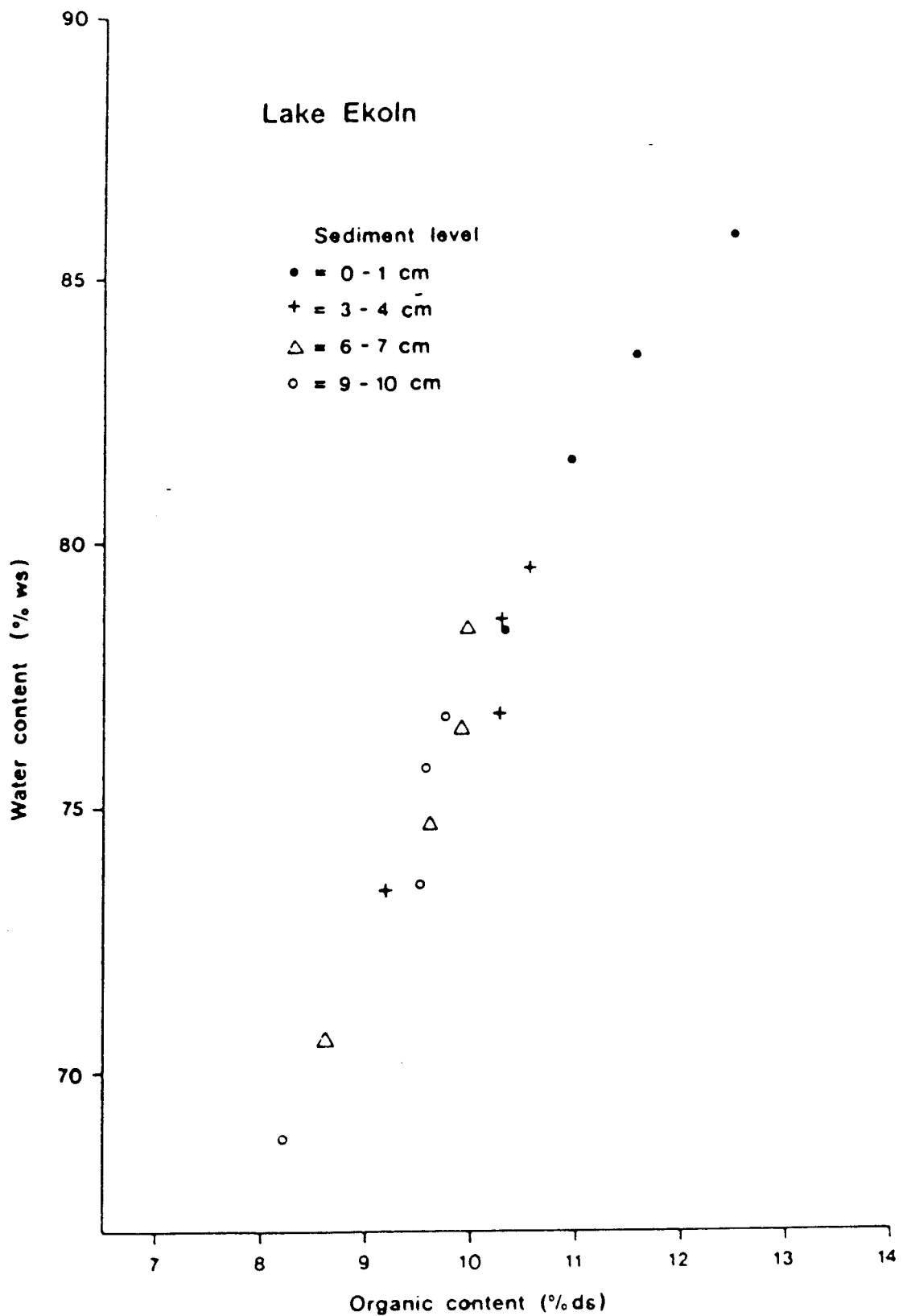


Figure 3

Relationship between water content and organic content (loss of ignition) at different sediment depths in Lake Ekoln (Håkanson 1977a)

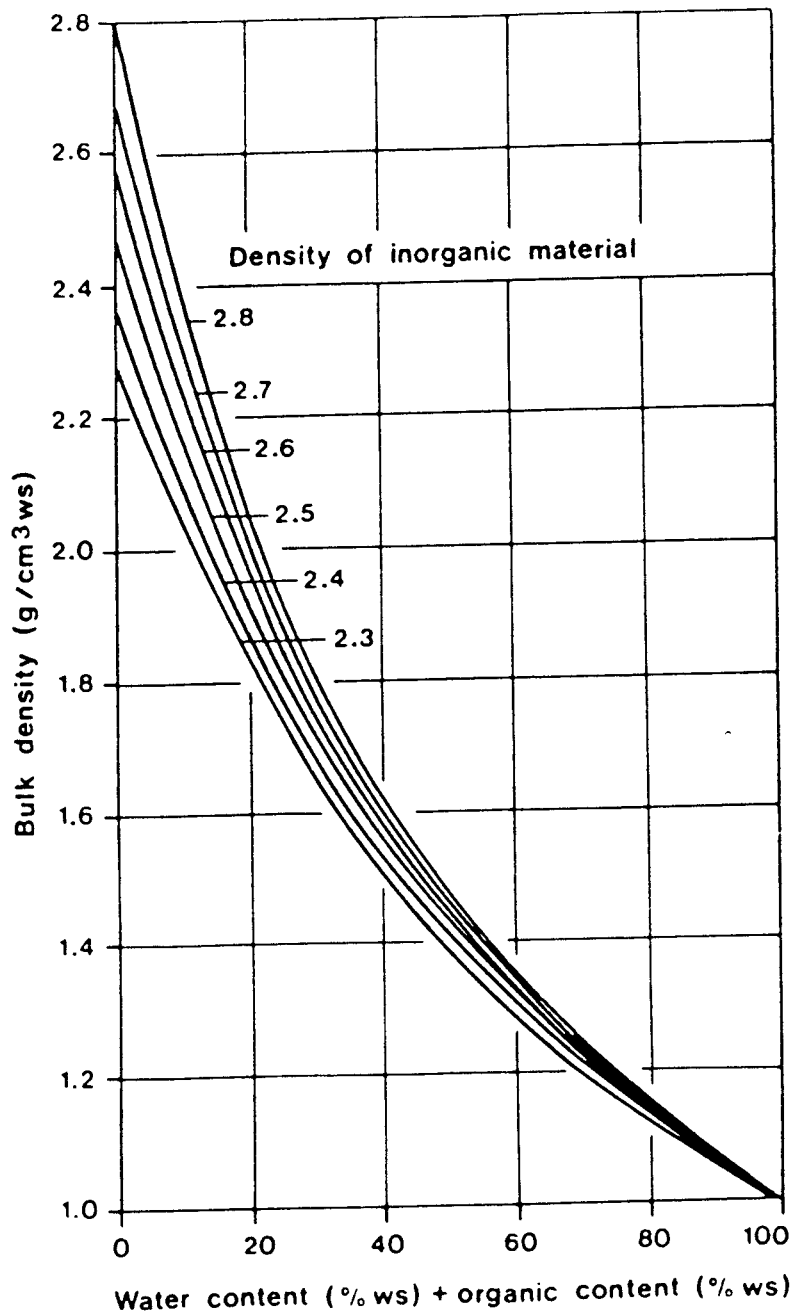


Figure 4

Nomogram illustrating the relationship between water content, organic content, bulk density and density of inorganic material (Axelsson and Håkansson 1971)

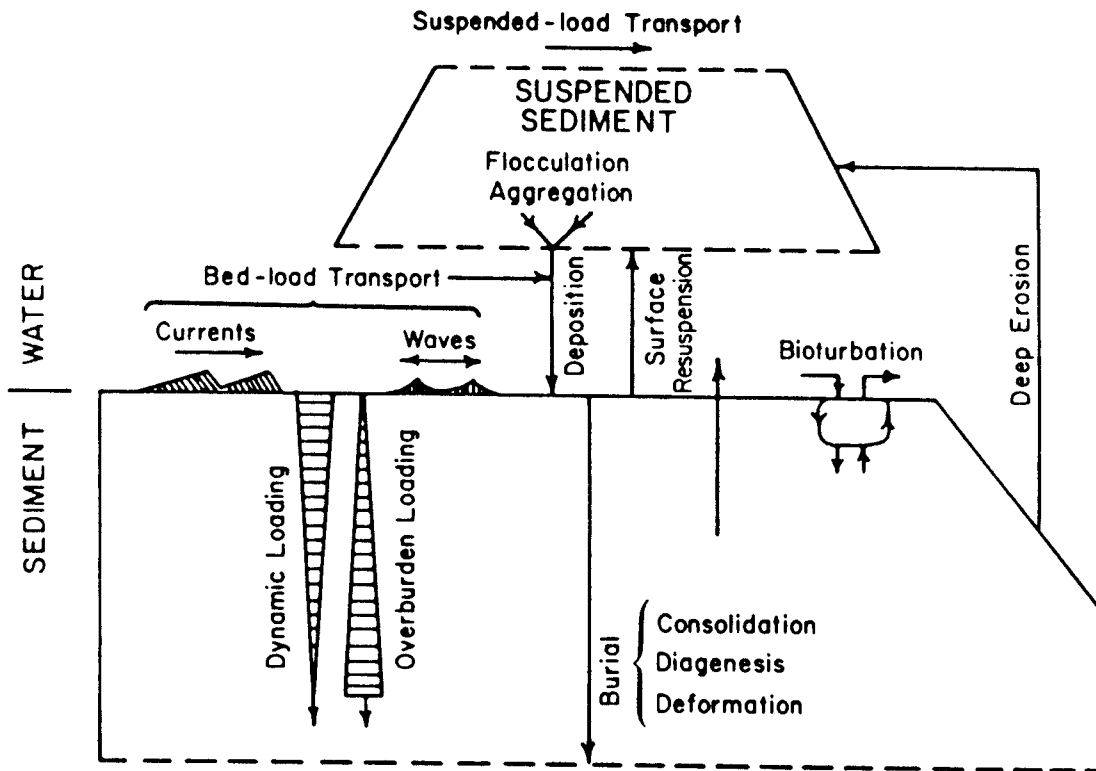


Figure 5

Benthic boundary sedimentary processes. From Richards (1976)

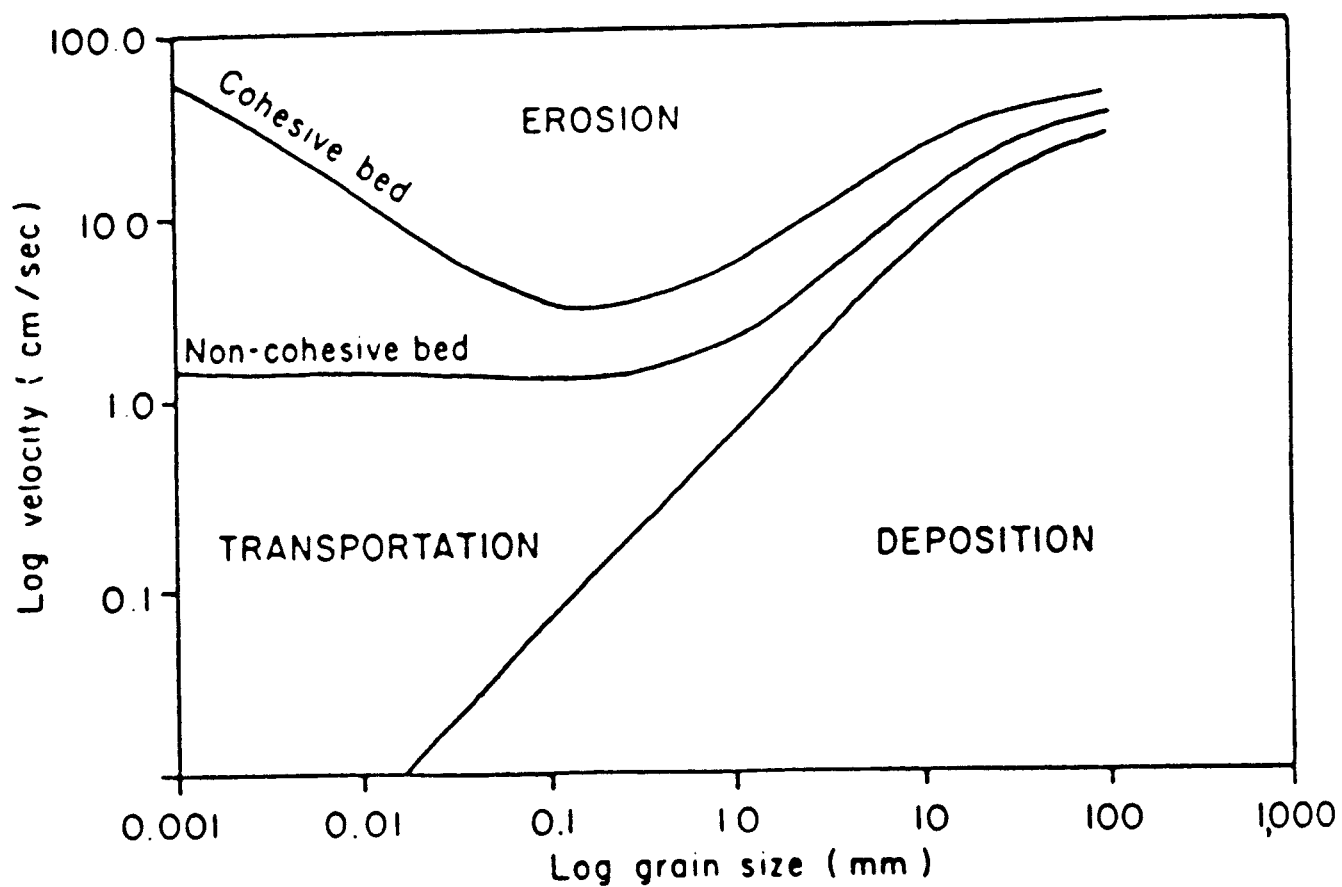


Figure 6

Hjulstroms graph showing the critical velocities required to erode, transport and deposit sediments of varying grades. (After Sundborg, 1956.)

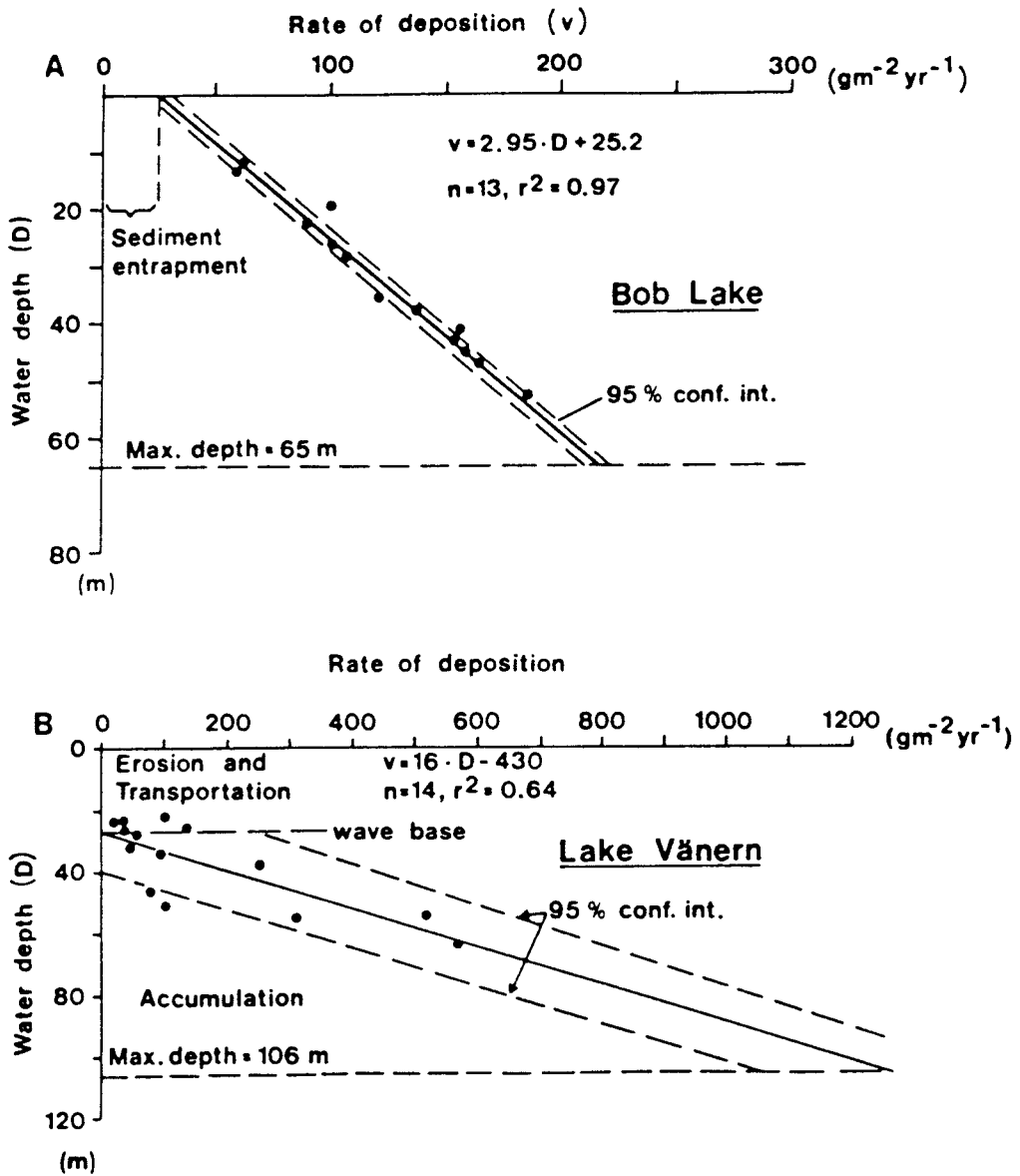


Figure 7

The relationship between rate of deposition and water depth: **A** In a small lake, Bob Lake, Canada (redrawn from Evans and Rigler 1980). **B** In a large lake, Lake Vänern, Sweden (Håkanson 1975)

Table 1

Chemical classification of elements in lake sediments (Kemp et al 1976, Håkanson 1977d)

-
1. Major elements (Si, Al, K, Na and Mg), make up the largest group of the sediment matrix.
 2. Carbonate elements (Ca, Mg and CO₃-C), constitute the second largest group in sediments, about 15 % of the materials by weight.
 3. Nutrient elements (org-C, N and P), account for approximately 10 % in recent lake deposits.
 4. Mobile elements (Mn, Fe and S), make up about 5 % of the total sediment weight.
 5. Trace elements (Hg, Cd, Pb, Cu, Zn, Ni, Cr, Ag, V, etc), the smallest group, accounting for less than 0.1 % of the sediments.
-

Table 2

Sediment growth in three eutrophic Swedish lakes between 1963 and 1975 calculated from Edberg (1980)

| Lake | Depth (m) | Sediment growth (mm yr ⁻¹) | |
|-----------|-----------|--|---------------|
| | | deep parts | shallow parts |
| Norrviken | ~ 9 | 8 - 10 | 3 - 4 |
| Ramsjön | 1.5 - 2 | 8 - 9 | 3 - 5 |
| Ekoln | ~ 17 | 8 - 11 | |

Table 3

Accumulated amounts of sediment (kg m^{-2}), integrated over 25-year intervals, and the total amount integrated over 125 years. L O I % refers to the loss of ignition in per cent as averaged over 125 years. Asterisk = approximate value. From El-Daoushy and Johansson (1983).

| Period, years | Lake Skärvsjön | | Lake Björken | Lake Väster- Täckelsjön | Lake Tussjön |
|--|----------------|-------|-----------------|----------------------------|-----------------|
| | S1 | S2 | | | |
| Sediment ($\text{kg} \cdot \text{m}^{-2}$) | | | | | |
| 0- 25 | 1.00 | 0.85 | 1.40 | 2.55 | 0.65 |
| 25- 50 | 1.10 | 0.85 | 1.70 | 2.80 | n.d. |
| 50- 75 | 1.15 | 1.00 | 1.70 | 3.05* | n.d. |
| 75-100 | 1.05 | 0.85 | n.d. | 3.15* | n.d. |
| 100-125 | 1.05 | 0.75* | n.d. | n.d. | n.d. |
| 0-125 | 5.30 | 4.30 | 8.15* | 15.15* | $\cong 4.55^*$ |
| L.O.I.% | | | | | |
| average (0-150) | 30 | 30 | 25 | 30 | 40 |

Table 4

Sediment reworking capacities of marine and freshwater benthic invertebrates. From Evans (1982).

| Species | Biotope | Locations | Reworking rate | Ref |
|------------------------------|-------------------------|-----------|---|------------------------|
| <u>Polychaete worms</u> | | | | |
| Heteromastus filiformis | marine intertidal | mud | 100 ml m ⁻² day ₁ ⁻¹ = 4 cm sed yr ⁻¹ | Cadeé (1979) |
| Pectinaria californiensis | marine subtidal | mud | 1 kg m ⁻² month ⁻¹ (dry wt) | Nichols (1974) |
| Clymenella torquata | marine subtidal | mud | 274 ml ind ⁻¹ yr ⁻¹ | Rhoads (1963) |
| Clymenella torquata | marine subtidal | mud | 96-246 ml ind ⁻¹ yr ⁻¹ | Magnum (1964) |
| Pectinaria gouldii | marine subtidal | mud | 400 ml ind ⁻¹ yr ⁻¹ | Gordon (1966) |
| <u>Oligochaete worms</u> | | | | |
| Limnodrilus sp | freshwater profundal | mud | 2 cm sed ind ⁻¹ yr ⁻¹ | Davies et al (1974) |
| <u>Bivalves</u> | | | | |
| Yoldia limatula | marine subtidal | mud | 250-400 ml ind ⁻¹ yr ⁻¹ | Rhoads (1963) |
| Nucula annulata | marine subtidal | mud | 365 ml ind ⁻¹ yr ⁻¹ | Young (1968) |
| <u>Crustaceans</u> | | | | |
| Callianassa | marine subtidal | mud | 75 cm thick layer transported to the surface ind ⁻¹ yr ⁻¹ | Warme (1965) |

1984-07-03

Karin Andersson

CHEMICAL PROPERTIES OF LAKE SEDIMENTS AND PEAT
OF IMPORTANCE FOR TRACE METAL BEHAVIOUR

ABSTRACT

A trace metal released into a lake, river or sea recipient may be expected to sooner or later reach a sink in the sediments. Evolution of the recipient may however eventually turn the former sediments into farming land or a peat bog, where a release of the metal may occur.

The chemical environment may change considerably during this time and a review of the present knowledge of interstitial water and solid phase chemistry in sediments and peat is given in this report.

Some important parameters are:

pH - may vary from 3.5 for some peatlands to over 8 in other peat types and in sediments.

Redox potential - both anoxic and oxic environments may be found.

Ionic strength - depends both on water supply (rain water to Baltic sea water) and reactions in sediment or peat (usually higher ionic strength than in surrounding water phase).

Complex formers - high contents especially of organic complex formers (humic substances).

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1 INTRODUCTION

A trace metal which is released into a recipient (lake, river or sea) will be transported through different pathways until it reaches a more or less final sink in the sediments. Evolution of the recipient may however eventually turn the lake or bay into a agricultural land or a peat bog.

The chemical environment for the metal may be expected to undergo a series of changes during the evolution, and may thereby turn the sink into a source, i.e. release the fixed metal.

The time span for this kind of change will be of the order of thousands of years, and predictions of the long term fate of metals during the evolution have to be based on our present knowledge of systems existing in different stages of evolution.

Here, a review is given of the present knowledge of the chemistry of the interstitial water and of the solid phase in sediments and peat. Complexation and sorption processes for actinides and fission products as well as for some heavy metals have also been included.

One way in which analogous phenomena in nature may be studied is through the enrichment of metals, e.g. uranium, thorium and lead, in peat bogs. Some examples of sites where this has occurred are given.

Since the aim of the present study is to provide information in order to be able to predict the transfer of radionuclides released into the biosphere from deep rock repositories of high

level nuclear waste, the main emphasis has been focused on the behaviour of actinides and fission products. Other trace metals, e.g. heavy metals, have however been studied in sediments and peat for a long time. These may show many similarities, especially to fission products but also to actinides, as regards their chemical properties; for this reason heavy metal data have been included to some extent in the present review.

2 THE CHEMISTRY OF SEDIMENTS

The chemical conditions within a sediment are determined by complicated interrelations of reactions occurring within the different phases in the sediment as well as between these. Not only equilibrium conditions have to be considered, since a decomposition of organic matter is continuously going on in the sediments. In additions the inorganic reactions may be governed by slow reaction kinetics.

Some parameters of importance to trace metal behaviour in the sediments have been studied by various investigators - pH, Eh, ionic strength, content of complex formers as well as properties of the sorbing solids are among the most important. The sediments consist of organic and inorganic solids and an interstitial water phase which has a composition different from that of the overlaying lake water. The concentration gradient between sediment and lake water may cause a diffusion of solutes, usually from sediment to lake water.

2.1 Organic compounds in sediments

The organic compounds constitute a very important component both in sediments and in overlaying water columns, influencing factors such as oxygen content, carbon dioxide content and redox potentials. This in turn controls solubilities e.g. of phosphorus, iron and manganese. The redox conditions are also of fundamental importance to the biological activities.

The preservation and interconversion of organic matter is not only a biological activity but also a function of morphology, trophic state, stratification and oxygen content. Seasonal

density stratifications may lead to a depletion of hypolimnetic oxygen, affecting the decomposers in the water column as well as the benthic animals (BAR 78).

The concentration of organic carbon is generally low in the water column (10^{-3} to 10^{-2} g/l), while in the sediments concentrations in the order of 10 g/l are encountered. The highest organic concentration is found at the sediment surface, with a decrease deeper down due to decomposition (AVN 84).

The organic compounds which are of major importance to the behaviour of trace metals in soils, peat bogs, lake and groundwater as well as in sediments are the complex formers defined as humic substances. These constitute a heterogeneous group of substances with some common properties. The complex forming capacity is due to the presence of carboxylic, hydroxy and phenolic groups. Four different kinds of humic substances are defined by the solubility properties: humic acid is soluble in alkali but not in acid, fulvic acid is soluble in both alkali and acid, humatomelanic acid is the fraction of humic acid which is soluble in alcohol and humin is insoluble in alkali (OLO 83).

The properties of humic acid vary according to its origin. In general the carbon content of lake and marine humic acids is lower and their H/C and N/C ratios are higher than those of soil humic acid. The molecular weights may vary for all types from 700 up to over 200 000. Components weighing over 100 000 are however more common in lacustrine and marine humic acids than in those from soil (ISH 72).

The molecular weight distribution is different for organics in interstitial water, and humic and fulvic acid. In Table 1 the various fractions found in Great Lakes sediments are given (KEM 74:2). It is possible that the water soluble organic matter in the interstitial water is the breakdown product from the larger molecular weight compounds which undergo transformations. The complexing properties of humic compounds are treated in more detail in chapter 4.

Table 1. Molecular weight distribution of organic compounds in various fractions of Great Lakes sediments acc. to Kemp (KEM 74:2)

| Fraction | Molecular weight | | |
|---------------------|------------------|------------|----------|
| | <700 | 5000-10000 | >200 000 |
| Interstitial water | 70-80% | - | - |
| Fulvic acid extract | 20-23% | 23-35% | 18-29% |
| Humic acid extract | - | 27-48% | 25-51% |

2.2 Nutrients

Among the nutrients phosphorus is an important element, participating in many reactions within the sediments, including complex formation with trace metals.

The total amount of phosphorus in lake sediments varies between 0.6 and 5 mg/g dry weight and there does not seem to be any close relationship between the trophic level of the lake and the phosphorus content. The greater part of the phosphorus in a lake ecosystem is bound to sediment particles and sorption may occur on iron(III)- and aluminum(III)-hydroxides, clays, calcite and humic substances containing metal ions.

In an oligotrophic lake most of the phosphorus input is deposited in the sediments, but with an increasing trophic level the interactions become more complex. During certain periods the release of phosphorus may exceed the deposition and outflow will occur both to anaerobic and well aerated water. A dissolution of iron and phosphorus is observed when iron(III) is reduced at potentials lower than 200 mV. There are however indications that iron bound to humic compounds is less sensitive to reduction.

A high pH may cause the release of phosphorus bound to iron and aluminum, while in calcareous sediments the formation of solid hydroxy-apatite increases with pH (BOS 82). There also seem to be interrelations between the phosphorus release and nitrate (BOS 82).

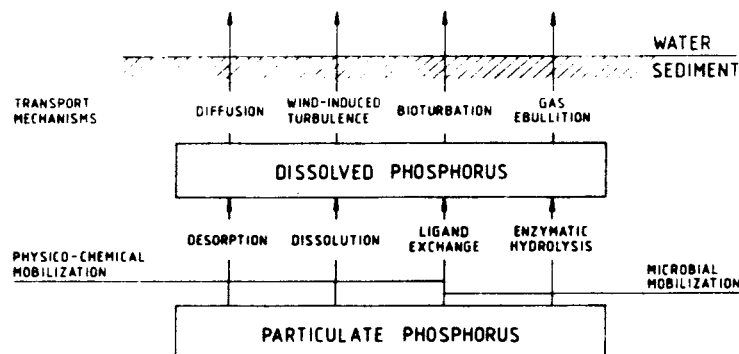
Table 2 and Figure 1 show some mechanisms and parameters affecting the phosphorus.

The many forms in which phosphorus may exist in sediments thus create a very complex situation as regards deposition and release reactions.

Table 2. Effects of important environmental factors on phosphorus mobilization acc. to Boström (BOS 82)

| Environmental parameter | Effect on phosphorus mobilization |
|-------------------------|---|
| Redox potential | Iron-bound phosphorus is released at potentials below 200 mV when iron (III) is reduced to iron (II). |
| pH | An increase in pH decreases the phosphorus-binding capacity of iron and aluminum compounds, primarily due to ligand exchange reactions where hydroxide ions replace phosphate. Calcite and apatite formation at higher pH-values increase the phosphorus-binding capacity of calcium. |
| Temperature | An increase in temperature gives primarily indirect effects due to increased bacterial activity, which increase oxygen consumption and decrease the redox potential. The production of phosphate-mobilizing enzymes and chelating agents might increase accordingly. |
| Equilibrium criteria | Affects adsorption-desorption and dissociation of precipitates. |
| Chelating agents | Replace phosphate from salts with calcium, iron and aluminum. Chelating agents can be produced by bacteria and algae or occur as a pollutant. |

Figure 1. Important processes of phosphorus release from lake sediments acc. to Boström (BOS 82)



2.3 Trace metals

The total content of metal ions in sediments has been studied by several investigators.

Sediment cores from Lake Como, Italy were sliced and analysed for grain size, mineralogy and chemical composition. The sampling points were chosen so as to represent lithological differences in the drainage areas: intrusive bodies, metamorphic rocks, ophiolites, limestones, dolomites etc. Generally a surface enrichment of Cr, Cu, Pb and Zn was encountered. These elements had higher contents than natural (BUG 81). Elemental analysis of sediments from Chautauqua lake, NY by NAA (Neutron Activation Analysis) was performed and the result compared with data for the surrounding bedrock. Eu, Na, Mn, K, Br, As, Ga, La, Hf, Cs, Tb, Sc, Fe, Ta and Sb were determined. The lake sediments were found to be enriched in Na, Mn, Br, As, Hf, Tb, Ta, and Sb. There was also a relationship for many elements between their concentrations and the clay fraction of the sediment, possibly due to the higher cation capacity of the clay minerals (HOP 76).

2.4 Mineralogy

The minerals in sediments may be of three different origins:

- Allogenic, i.e. coming from outside the lake and supplied by rivers, shore erosion etc. Among these minerals, silicates (including clays) and carbonates are the most common.

- Endogenic, i.e. precipitates formed in the lake water. Among these are calcite and iron(III) compounds as well as diatoms

with sorbed species such as silica and others.

- Authigenic, i.e. formed within the sediments due to changes in chemical and/or physical properties.

In Table 3 a list of minerals likely to be found in lake sediments is given (HÅK 83). A mineralogy that indicates allogenic sources of the minerals has e.g. been observed in Lake Como, Italy where the following minerals were identified in a 27 cm sediment core: quartz, muscovite, illite, chlorite, plagioclase and dolomite (BUG 81).

Important authigenic minerals are phosphates, e.g. vivianite, reddingite and anapaite. These are the stable and most probable phosphate minerals in reducing environments, and are considered to constitute the buffering mechanisms for Great Lakes sediments, regulating both the levels of phosphorus in the interstitial waters and the release of phosphorus to the overlying lake waters (NRI 74). In Greiffensee, Switzerland it has however been shown that the phosphate minerals formed are not the most stable thermodynamically, and kinetics here seem to be of great importance for mineral formation (EME 78).

Sulfides are also formed authigenically. This is considered to be a process largely controlled by biological processes (NRI 68). The sulfides are responsible for the dark colour of the sediments and treatment with dilute acid may remove the dark colour and simultaneously release H₂S (DOY 68).

Table 3. Minerals from lake sediments acc. to Håkansson (HÅK 83)

| Mineral | Type of source | | |
|--|----------------|-----------|------------|
| | Allogenic | Endogenic | Authigenic |
| Non-clay silicates | | | |
| Quartz - SiO_2 | X | | |
| Potash feldspar - KAlSi_3O_8 | X | | |
| Plagioclase - $(\text{Na}, \text{Ca}) (\text{Al}, \text{Si}) \text{Si}_2\text{O}_6$ | X | | |
| Mica - $\text{K} (\text{Mg}, \text{Fe}, \text{Al})_3 \text{AlSi}_3\text{O}_{10} (\text{OH})_2$ | X | | |
| Amphibole - $(\text{Ca}, \text{Mg}, \text{Fe}, \text{Al})_{2.5} \text{Si}_4\text{O}_{11} (\text{OH})$ | X | | |
| Pyroxene - $(\text{Ca}, \text{Mg}, \text{Fe})_2 \text{Si}_2\text{O}_6$ | X | | |
| (Other heavy minerals, $\rho > 3.0$) | X | | |
| Opaline silica (diatoms) | | X | |
| Clays | | | |
| Illite - $\text{K}_{0.8} \text{Mg}_{0.35} \text{Al}_{2.26} \text{Si}_{3.43} \text{O}_{10} (\text{OH})_2$ | X | | |
| Smectite - $\text{X}_{0.3} \text{Mg}_{0.2} \text{Al}_{1.9} \text{Si}_{3.9} \text{O}_{10} (\text{OH})_2$ | X | | |
| Chlorite - $\text{Mg}_3 \text{Al}_2 \text{Si}_3 \text{O}_{10} (\text{OH})_6$ | X | | |
| Kaolinite - $\text{Al}_2 \text{Si}_2 \text{O}_5 (\text{OH})_4$ | X | | |
| Mixed clays, vermiculite - intermediate | X | | ? |
| Palygorskite - $(\text{Ca}, \text{Mg}, \text{Al})_{2.5} \text{Si}_4 \text{O}_{10} (\text{OH}) \cdot 4\text{H}_2\text{O}$ | X | | ? |
| Nontronite - $\text{X}_{0.5} \text{Fe}_2 \text{Al}_3 \text{Si}_{3.5} \text{O}_{10} (\text{OH})_2$ | X | | X |
| Carbonates | | | |
| Calcite - CaCO_3 | X | X | x |
| Dolomite - $\text{CaMg}(\text{CO}_3)_2$ | X | | ? |
| Aragonite - CaCO_3 | x | X | |
| Mg-calcite - intermediate | | x | X |
| Rhodochrosite - MnCO_3 | | | X |
| Monohydrocalcite - $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ | | X | ? |
| Siderite - FeCO_3 | ? | | ? |
| Fe-Mn oxides | | | |
| Goethite, Lepidocrocite - FeOOH | X | x | X |
| Magnetite - Fe_3O_4 | X | | |
| Hematite, maghemite - Fe_2O_3 | X | | ? |
| Birnessite - $(\text{Na}, \text{Ca}) \text{Mn}_7\text{O}_{14} \cdot 3\text{H}_2\text{O}$ | ? | | X |
| Todorokite - $(\text{Na}, \text{Ca}, \text{K}, \text{Ba}, \text{Mn})_2 \text{Mn}_5\text{O}_{12} \cdot 3\text{H}_2\text{O}$ | ? | | X |
| Psilomelane - $(\text{Ba}, \text{K}) (\text{MnO}_2)_{2.5} \cdot \text{H}_2\text{O}$ | | | X |
| Ilmenite - FeTiO_3 | X | | |
| Phosphates | | | |
| Apatite - $\text{Ca}_5(\text{PO}_4)_3 (\text{OH}, \text{F})$ | X | | x |
| Vivianite - $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ | | | X |
| Ludlamite - $(\text{Fe}, \text{Mn}, \text{Mg})_3 (\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ | | | X |
| (?) lipscombite - $\text{Fe}_3(\text{PO}_4)_2 (\text{OH})_2$ | | | X |
| (?) phosphoferrite - $(\text{Mn}, \text{Fe})_3 (\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ | | | X |
| (?) anapaite - $\text{Ca}_3 \text{Fe} (\text{PO}_4)_3 \cdot 4\text{H}_2\text{O}$ | | | X |
| Sulfides | | | |
| Mackinawite - FeS_2 | | x | X |
| Pyrite - FeS_2 | X | | x |
| Griegite - Fe_3S_4 | | | X |
| Sphalerite - ZnS | | x | |
| Fluoride | | | |
| Fluorite - CaF_2 | | | X |

Print size is varied to illustrate the frequency of occurrence. X in formulas refers to monovalent cation exchange

2.5 Redox conditions

The redox potential is an important parameter, determining the valence state and thus the chemical properties of many trace metals. It is closely related to the oxygen content, and sediments formed under varying oxygen conditions depending on the time of the year sometimes show a laminated structure which can be seen visually as alternating dark (sulfide) and light layers and can also be measured with a platinum electrode. The electrode potential decreases with depth and a column of sediment may be gray or black at depth and brown, yellow or orange at the surface near the zone of oxygenated water (DOY 68). A typical platinum electrode potential gradient in a sediment core and the overlying water column is shown in Figure 2 (MOR 71). The pS^{2-} has also been determined, Figure 3. Both the profiles show large gradients in the upper 20 cm and constant (or undetectable) values in the lower portion of the core. The boundary corresponds to the general appearance of the sediment which changes from black to light gray in this region (EME 76).

Sulfur is an important element in sediment chemistry as the sulfur compounds are redox sensitive. In lake sediments sulfide dissolved in the interstitial water, acid volatile sulfide, elemental sulfur, organic sulfur and sulfates have been identified (NRI 68).

Figure 2. Platinum electrode potential across sediment/water interface in "undisturbed" cores from the deepest basin of Windermere during three seasons, acc. to Mortimer (MOR 71)

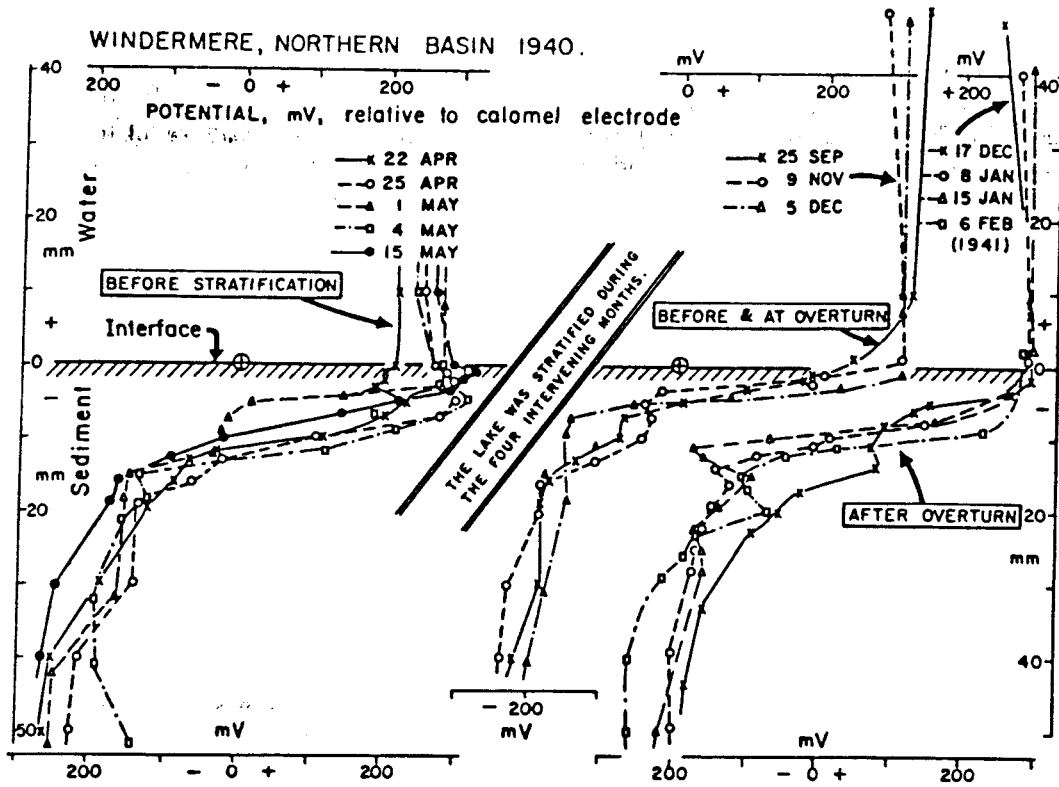
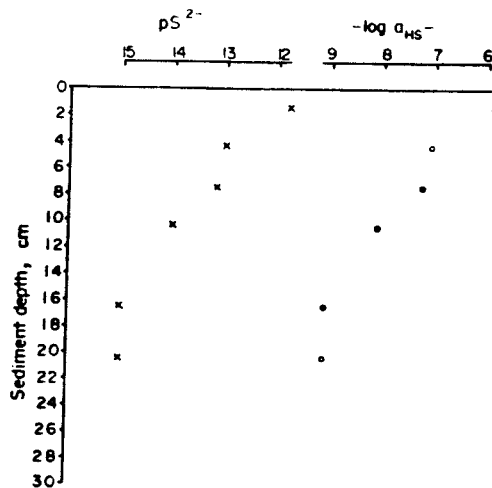


Figure 3. Sulfide activity as a function of depth in a lake sediment core acc. to Emerson (EME 76)



2.6 Interstitial water composition

The composition of the interstitial water in lake sediments has been investigated. Usually the water has been extracted by pressing the cores, but in some cases the water phase after centrifuging has been used.

pH. Emerson et al studied the pH of sediment cores from Greifensee by inserting glass electrodes directly into the core. The pH was found to be quite constant (= 7.05) with depth, cf. Figure 4 (EME 76). The pH of sediments from Seneca Lake, NY, was determined at different depth. This is a lake of glacial origin. The pH down to 20 cm depth varied very little (6.8-7.1) and was equal to the value observed in the overlying lake water. In some cases slight decreases with depth were observed (HAR 67).

Na. The Na content in interstitial water in sediment cores from Greifensee, Switzerland showed a decrease down to 50 cm. This may partly be explained by an increased salting of the roads since the mid 60's (EME 76).

In sediment cores from Lake Eire, the pore water was analyzed, in one case down to 180 cm depth, cf. Tables. An enrichment in Na compared to the lake water was observed. In some cases a gradient of Na (increase with depth) was observed (NRI 74).

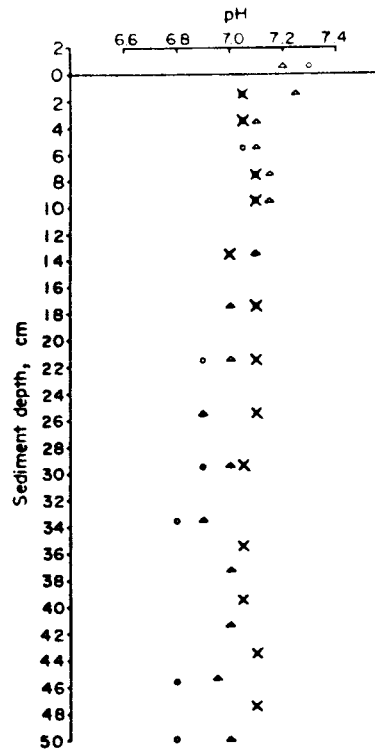
K. Likewise for K there was a slight increase with depth in some Lake Eire sediment cores (NRI 74).

Ca. The content of calcium also increased with depth in Greifensee sediments, but the large

increase in the first few centimeters was followed by a moderate maximum at 6-10 cm. At larger depths the profile was vertical (EME 76).

In Lake Eire sediments there was a general increase with depth for Ca (NRI 74).

Figure 4. pH of the interstitial water of a lake sediment core. X = results from inserting the electrode directly into the sediment, O = data from the supernate solution after centrifuging, Δ = first reading for the alkalinity Gran titration acc. to Emerson (EME 76)



Mg. In Greifensee sediments no gradient of Mg could be found (EME 76).

In Lake Eire, there was also a gradient of Mg. This was not however the case for all the sediment cores (NRI 74).

Mn. No gradient of Mn was found in Greifensee, cf. Figure 5 (EME 76). The concentration of Mn in Lake Eire was highly variable but tended to increase with depth (NRI 74).

Fe. A very large gradient of Fe in the pore water of Greifensee sediments was found, cf. Figure 5 (EME 76).

In lake Eire, the Fe content was highly variable but tended to increase with depth (NRI 74).

P. A large gradient of phosphorus was observed in Greifensee sediments, c.f. Figure 5 (EME 76).

In lake Eire no apparent P-gradient was observed (NRI 74).

N. No evident gradient in N was found in Greifensee sediments (EME 76).

Si. In a study of the silica content in river, lake and organic bog sediments, very high silica concentrations were found in river and organic bog sediments at 6 cm below the surface. This was associated with a low pH. An attempt was made to explain this in terms of decomposition of organic matter (HAR 67).

Cl. Chloride was also enriched in river, bog and lake sediments and the gradient was, as for silicate, confined to the top layer of the sediment. Below 8 cm there was a high and constant concentration (HAR 67).

Figure 5. Dissolved P, Fe, and Mn in interstitial water of lake sediment core acc. to Emerson (EME 76)

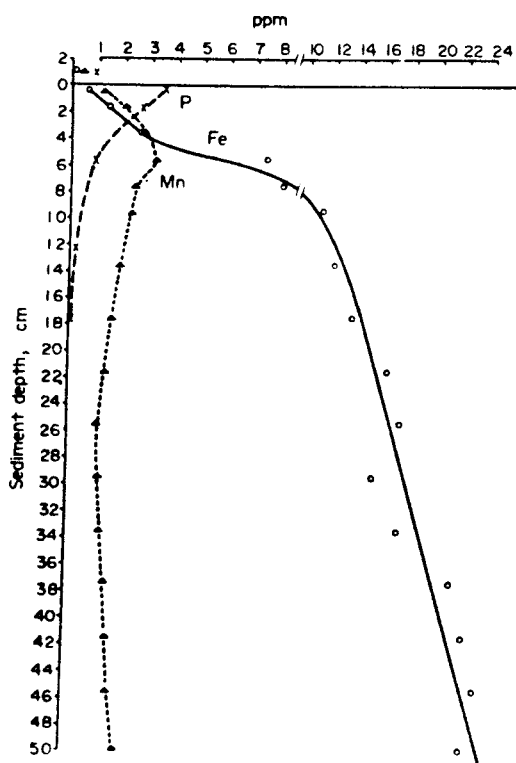


Table 4 gives a review of composition data for some natural waters. The total amount of dissolved species is of the same order of magnitude in sediment interstitial water as in shallow groundwater. The quoted sediment data are however for freshwater lakes. The pore water composition in Baltic sea or ex Baltic sea sediments may be different, considering the much higher ionic strength in Baltic sea water.

A concentration in the water phase as regards Na, K, Mg, Ca, Mn, Fe and possibly N seems to occur in lake sediments. A larger amount of material and also data for interstitial water from Swedish lakes would however be required to draw further conclusions on the pore water composition development.

Potential complex formers among the inorganic ions are phosphates, nitrates, carbonates and silicates. Silica, as well as Fe-, Al- and Mg-hydroxides, may also act as a colloidal sorbing agent. Unfortunately, the studies on pore water composition encountered in the literature do not include carbonates and sulfates.

Table 4. Concentrations of major ions in some types of natural water.
Data in mg/l.

| | Rain water ^d | Shallow ^d groundwater | Intermediate ^d groundwater | Lake water ^a | Lake sediment ^{a,b} 0 - 6 cm | Lake sediment ^{a,b} > 6 cm | Sea water ^d | Baltic sea ^d water | Peatland ^e waters |
|--------------------------------|-------------------------|-------------------------------------|--|-------------------------|--|--|------------------------|----------------------------------|---------------------------------|
| Na | 0.3-20 | 2-25 | 10-100 | 1.3-15 | 2.3-21 | 4.4-36 | 10560-10766 | 1620-4980 | 1.3 -40 |
| K | 0.1-4 | 0.5-5 | 1-5 | 0.5-1.35 | 1.2-4.6 | 1.5-4.8 | 380-399 | 54-180 | 0-5 |
| Mg | 0.1-0.5 | 0.5-10 | 5-20 | 2.7-10 | 3.7-16 | 4.9-18 | 1272-1292 | 186-600 | 0.1-43 |
| Ca | 0.5-5 | 5-50 | 25-50 | 13-61 | 26-109 | 30-109 | 380-399 | 70-190 | 1.2-110 |
| Mn | | | 0.1-0.5 | 0.002-0.7 | 0.4-7.9 | 0.9-8.9 | 400-413 | | 0.01-0.6 |
| Fe | | 0-0.5 | 1-20 | 0.005-0.1 | 0.3-7.4 | 1.2-22.8 | <0.02 | | 0-9 |
| Cl ⁻ | 0.1-20 | 5-20 | 5-25 | 16-118 | 18-129 | 10-152 | 18980-19353 | 2860-8960 | 1-50 |
| NO ₃ ^{-c} | 0.1-4 | 0.1-5 | 0.1-0.5 | 6.6 | 6.6-12.4 | 12.0-13.3 | <0.7 | | 0-18 |
| HCO ₃ ⁻ | <1 | 60-250 | 60-400 | | | | 140 | 73-140 | 1-420 |
| SO ₄ ²⁻ | 0.1-5 | 0.5-25 | 1-25 | | | | 2650-2712 | 410-1260 | 2-180 |
| PO ₄ ^{3-c} | | | 0.01-0.1 | 0.6-2.8 | 0.1-14.4 | 0.07-2.8 | <0.1 | | |
| SiO ₂ | <1 | | 5-30 | 0.46 | 1.5 | 2.4-2.6 | 0.1-7 | | |
| Σ | 2-60 | 75-400 | 100-600 | 41-216 | 60-323 | 67-370 | 35000 | 5273-16310 | 6.6-875 |
| pH | 4-6 | 5-8.2 | 7.2-8.5 | 7.1-8.0 | 6.9-8.0 | 6.8-7.6 | 8.1 | 8.1 | 3.5-7.1 |

^a Lake water and lake sediment data based on measurements in Seneca Lake, N.Y., Greifensee, Switzerland, and Lakes Eire, Ontario, Michigan, Huron and Superior, according to (HAR 67), (EME 76) and (NRI 74).^b Sediment = interstitial water.

^c Total N and P data recalculated to NO₃⁻ and PO₄³⁻, respectively.

^d Data for rain water, groundwater and sea water from (DYR 80), (LAU 83) and (GOF 77)

^e Data for peatland waters from (CLY 83), (TOL 74), (LAR 76), (SCH 77), and (CHM 77)

2.7 Changes in chemistry with time

The changes in chemical properties of a lake sediment with time may be discussed using the distributions of elements observed in sediment cores.

In the interstitial water there is an increase in ionic strength with depth, a decrease in redox potential and very slight changes in pH.

Changes in total chemistry are mostly confined to the organic matter, which undergoes a continuous degradation due to biological activity as well as to changes in the chemical environment.

The degradation rate in sediments from 64 small and shallow lakes in the United States has been determined. For organic carbon the decay coefficient was of the same order of magnitude for all the lakes and around $4 \cdot 10^{-3} \text{ y}^{-1}$. The same value was observed for organic nitrogen. For phosphorus, which in contrast to carbon and nitrogen does not form volatile decomposition products, the changes with depth were not as obvious, even though a large fraction of the phosphorous in the sediment is organic. A similarity of the decay rates of organic carbon, nitrogen and phosphorous in lakes located in different climatic and geographic regions was however observed (AVN 84).

The changes with time in the organic content of sediment cores from Lake Haruna, Japan, have been studied. Sediment cores down to a depth corresponding to 1000 years have been analysed. In this environment the decomposition seems to be low, although the amount of extractable humic substances, which include both humic and

fulvic acids, decreases slightly with depth. In the humic acids there seems to be an increase in carbon content, C/H ratio, C/N ratio and colour intensity, and a decrease in proteinaceous material and in carbohydrate like material.

Three possible pathways for long term transformation of sedimentary humic acids are suggested: (1) sedimentary HA - soil HA - graphite, occurring in oxidizing environments, (2) sedimentary HA - coal - graphite, in pyrolytic conditions, (3) sedimentary HA - kerogen (or petroleum) - graphite, in reducing environments (ISH 72:2).

A comparison of sediment cores from Lake Washington taken in deep water in different parts of the lake in 1958/59 and 1968 and 70 was performed. During this interval the sewage effluent that had been causing eutrophication of the lake was diverted and the lake began to regress to a relatively unproductive state.

All the cores showed higher concentrations of organic matter, phosphorous and nitrogen in the top few centimeters than deeper down, but in general the higher surface values of the earlier material had decreased somewhat since they lay below the surface in the more recent cores (SHA 71).

3 THE CHEMISTRY OF PEAT LANDS

The chemical conditions vary between fen and bog. The bog obtains its water mainly from precipitation and it is thus poor in minerals. Bog vegetation is typically dominated by Sphagnum moss and ericaceous shrubs. Soils in bogs are usually undecomposed fibric peat overlying partly decomposed humic peat. The water may be quite acidic. Fens or minerotrophic peatlands are nourished by regional groundwater and are therefore ion rich and only slightly acidic to slightly basic. Fen vegetation is dominated by sedges (*Carex* spp.) and tall shrubs, e.g. birch (*Betula* spp.) alder (*Alnus* spp.) and willow (*Salix* spp.).

Many factors affect the chemistry of peat. Amongst the most important are the nature of the original plant matter, the supply of inorganic solutes, the activities of plants and animals and of microorganisms, environmental conditions (particularly temperature and the extent of waterlogging) and finally the age and history of the peat. These factors are of course not independent and there are marked vertical gradients associated with these.

In general our knowledge of the organic composition of peat is fragmentary, although its origin indicates that it will contain the same components as the plants which form the peat and decomposition products of these (CLY 83).

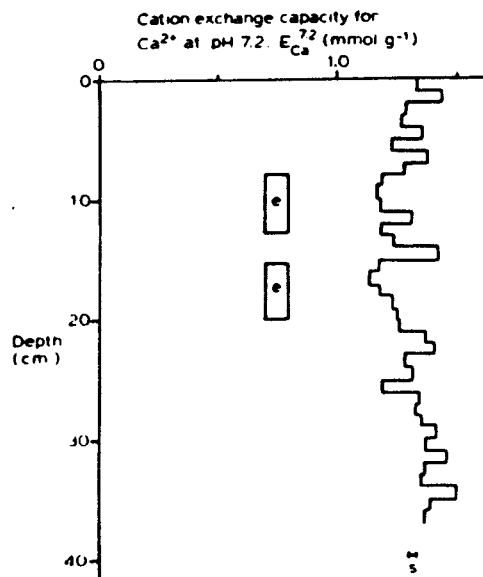
One important property of the peat is the cation exchange capacity. The cation exchange capacity (CEC) of organic soils is commonly in the range of 1 - 2 meq/g when measured at pH 7. For lower pH, the CEC will be lower. Considerable indirect

information exists to show that covalent bonding of divalent ions (Ca, Mg, Fe, Cu, Zn and Mn) occurs in peats and in isolated humic, fulvic and hymatomelanic acids. Monovalent ions are sorbed less strongly than divalent, and Mn^{2+} is more tightly held than Ca^{2+} (SIK 83)

For peats, the CEC may vary considerably and over short distances both horizontally and vertically. An example of a profile is given in Figure 6. Values of CEC from 0.07 meq/g to 1.9 meq/g have been observed in peats (CLY 83).

Buffer curves of acid peats generally have pK_a -values of about 6. This is weaker than predicted from consideration of the carboxyl group present, presumably a result of the formation of covalent bonded hydroxy complexes of iron and aluminum such that an increase of pH involves hydrolysis of these complexes rather than ionization of carboxyl groups (SIK 83).

Figure 6. Profile of cation exchange capacity of peat from Stordalen, Abisko, northern Sweden. Peat type *Sphagnum fuscum*, with some *Eriophorum* at points marked e. Acc. to Clymo (CLY 83)



3.1 Redox conditions

The "redox potential", i.e. the platinum electrode potential, is one indicator of the state of peat. There are difficulties in obtaining reproducible potentials and a "true" redox potential is probably never obtained. Within a certain set of peat cores the potential may however be a useful tool for determining the changes in redox conditions.

Three other features are commonly correlated with "redox potential" profiles: the position of the water table, the presence of sulfides and the oxygen concentration. There is usually a smell of hydrogen sulfide correlated to low redox potential and this usually occurs just below the ground water table, where the redox potential may decrease rapidly, cf. Figure 7 (CLY 83).

There is a need for concerted studies of chemistry and of microbiology at the same site in the field. There seem to be no published measurements of valence states and few of sulfide or oxygen concentrations in peat (CLY 83).

The redox potential and the formation of sulfides have also been discussed in chapter 2.

3.2 Organic compounds

The water in peat contains large amounts of organic substances originating from the decomposition of the peat-forming material. Among the best known of these are the humic substances. The characterization of humic substances was described in detail in chapter 2.

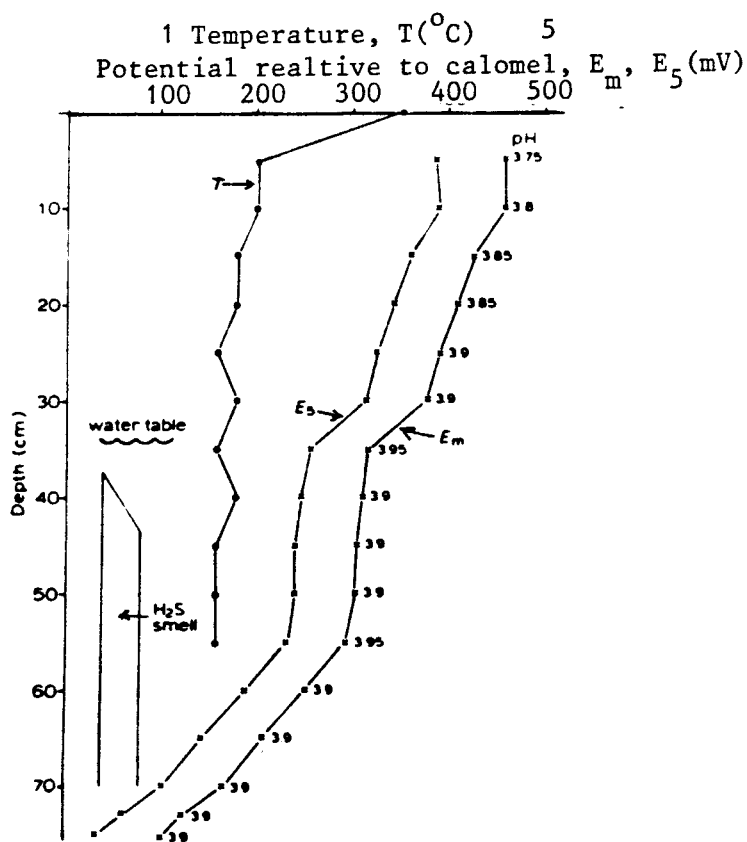
Natural humic substances originate from lignin or cellulose, which in a certain state of

decomposition lose their original character yielding compounds of the polyphenol type. The types of humic acids differ in the degree of polymerization, the nuclei and the type of reactive groups and linkage arrangements. However, due to their structure pattern the humic acids have many common and similar properties.

In Czechoslovak peat water the highest concentrations of humic acids were found in stagnant water bodies in high moor areas and in the pools left after peat exploitation. Values of 200 mg/l with a maximum of 600 mg/l were found in S and SW Bohemia (CHA 66).

In a study of the humic acids of peat water from Poland, molecular weights of 175 to 50 000 were found in the fulvic acid fraction, i.e. the fraction most readily soluble in water. The mean molecular weights were usually 2000 to 3000. There seemed to be the largest iron binding in the compounds with the highest molecular weights (CHM 77).

Figure 7. "Redox potential" profile on September 17 in Sphagnum fuscum peat near Abisko, northern Sweden. E_m = as measured; E_5 = calculated at pH 5^m using the temperature profile and pH value by each point. Acc. to Clymo (CLY 83)



3.3 Inorganic compounds

The concentration of inorganic substances in peat water is dependent on a number of conditions. One important parameter is the quality of the water supply. For oligotrophic bogs the supply is mainly precipitation and the mineral content of the water is thus low. The concentration in the precipitation of elements such as sodium, magnesium and chlorine varies and increases markedly towards the coast. Other elements in precipitation and dry deposition such as aluminium, manganese and iron probably derive from soil dust. Industrial and domestic gases, smoke, industrial dust, road dust, volcanic ash and extra-terrestrial particles (meteorites) may also contribute. Nitrogen may be supplied as ammonia gas, and absorbed directly by acid peat or fixed by the roots in the form of atmospheric nitrogen (CLY 83).

In minerotrophic bogs the main supply of mineral particles in soluble or suspended state is via surface drainage water, floodwater or underground water. Suspended mineral particles not only deposit together with the peat formed, but also enter the solution under the action of biochemical and other processes. Redox conditions also influence these processes (LAR 76).

It does not seem to be easy to draw distinct borders between the composition of fen and bog water. This was concluded from a study of 229 samples from 32 different mire complexes in Finland (TOL 74).

The value of pH of the water in peat lands may vary over a wide range. Values between 2.8 and 7.4 have been reported for different organic

deposits, although acid peats are more common than neutral ones (SIK 83). pH is a function of the type of peatland. It is low in oligotrophic bogs (3.5 - 5.9) while in eutrophic bogs it is higher (5.3 - 7.1) (LAR 76). In general fen peats have pH values near neutral as a result of calcium and magnesium ions, which together with bicarbonate raise the pH. Soils and sediments tend toward neutrality when flooded, regardless of the initial pH, mainly as a result of the consumption of hydrogen ions during reduction of iron through equilibrium reactions. Precipitates of FeCO_3 and FeS may also be formed during long-term water logging (SIK 83).

The mineralization also varies over a wide range. In oligotrophic bogs the water at 0.5 m depth may have a mineralization of 8-45 mg/l. The main ions are Ca^{2+} , Na^+ , K^+ , Cl^- and HCO_3^- . The total silica content is higher than that of Ca. In eutrophic bogs at the same depth the mineralization of the water is 60 - 500 mg/l. There are changes in mineralization both within the same bog complex and between different seasons. There are maxima in mineralization in the autumn and in the beginning of spring. Climatologic factors may also influence the mineralization (LAR 76).

In fens with pH about 7.5 the predominating cations are Ca^{2+} (totally about 0.5 mM, of which 1/20 is extractable) and Mg^{2+} (about 0.3 mM, with 1/50 extractable). In bogs with pH about 4.0 the total concentration of extractable Ca^{2+} and Mg^{2+} is not reduced by quite as much (CLY 83).

The relations between total concentrations of the major cations and the amount extractable in different extractants varies depending on the

cation studied. The sodium is bound to the peat to a lesser degree than Ca, Mg and K (CLY 83).

The relations between the contents of some metals (Ca, Mg, Zn and Fe) in moor waters and peat have been studied in Poland. For calcium and magnesium there was a connection, while for iron and zinc no such relation was observed. The iron and zinc in the waters were almost entirely fixed to the organic substances (CHM 77).

The statistical distribution of water characteristics has been analysed in a study of the water in 45 undisturbed Minnesota peatlands. Most of the data were log normally distributed. Only water temperature, pH, dissolved oxygen and fulvic acid were normally distributed. Mean values are given in Table 5 (CLA 83).

The ranges of water compositions in peatlands are given in Table 4 (p 21).

Table 5. Mean values of water quality characteristics in natural peatland runoff for five sampling periods in 1979 and 1980. Acc. to Clausen and Brooks, (CLA 83)

| Characteristic | Units | Peatland Type | | |
|------------------------------------|-------|---------------|------------|-------|
| | | Bog | Transition | Fen |
| No. of Samples | | 66 | 55 | 54 |
| Discharge | cfs | 2.51 | 9.31 | 9.31 |
| Temperature** | °C | 11.1 | 13.4 | 12.8 |
| Specific Conductance** | µS/cm | 45 | 72 | 171 |
| Dissolved Oxygen | mg/l | 6.4 | 5.4 | 5.6 |
| O ₂ Saturation | % | 56 | 50 | 53 |
| pH** | | 5.6 | 6.5 | 7.0 |
| Acidity as CaCO ₃ * | mg/l | 21.3 | 17.1 | 17.7 |
| Alkalinity as CaCO ₃ ** | mg/l | 10.1 | 28.8 | 74.5 |
| Color* | mg/l | 311 | 260 | 242 |
| Suspended Sediment | mg/l | 5.1 | 5.3 | 5.4 |
| Potassium | mg/l | 1.24 | 0.99 | 1.15 |
| Calcium** | mg/l | 6.76 | 11.57 | 27.27 |
| Magnesium** | mg/l | 2.37 | 3.93 | 7.90 |
| Aluminum** | mg/l | 0.55 | 0.25 | 0.25 |
| Iron | mg/l | 2.64 | 2.07 | 2.37 |
| Sodium** | mg/l | 1.84 | 1.32 | 2.74 |
| Manganese** | mg/l | 0.14 | 0.27 | 0.29 |
| Mercury | µg/l | 6 | 3 | 5 |
| Arsenic | µg/l | 2 | 3 | 3 |
| Selenium | µg/l | 1 | 1 | 1 |
| Total Phosphorus | mg/l | 0.06 | 0.05 | 0.08 |
| Total Kjeldahl Nitrogen | mg/l | 1.5 | 1.6 | 1.8 |
| Nitrate-N* | mg/l | 0.06 | 0.05 | 0.08 |
| Ammonia-N** | mg/l | 0.1 | 0.2 | 0.2 |
| Organic-N | mg/l | 1.4 | 1.4 | 1.6 |
| Humic Acid** | mg/l | 11 | 9 | 8 |
| Fulvic Acid | mg/l | 100 | 89 | 86 |
| Chemical Oxygen Demand** | mg/l | 118 | 104 | 97 |

*Significant difference among peatland types at $\alpha = 0.05$.

**Significant difference among peatland types at $\alpha = 0.01$.

3.4 Changes in chemistry with time

The basal and surface peats have high concentrations of silica, calcium and iron but the middle peat has lower concentrations. The same pattern, though less conspicuous, is shown by aluminum and manganese while potassium has a particularly pronounced surface peak. Other elements such as magnesium are more variable, but sodium and hydrogen ions tend to increase in concentration from the bottom to the top of the profile. Nitrogen and phosphorus have been more seldom measured. They have high concentrations at the surface but remain constant below it.

The high concentrations in the top 50 cm may reasonably be connected with the relocating activities of live plants and animals and with the change from aerobic to anaerobic conditions. The major changes occur in the top 50 cm or so even if some changes occur deeper down (CLY 83).

Even if an organic soil is waterlogged throughout the year, its profile will exhibit vertical gradients with respect to oxygen (redox potential) and temperature. In measurements of the dynamic changes in peat profiles (pH 2.7 - 3.1) in northern England over a one year period, a decreasing pH with depth was found. Differences have also been recorded before and after heavy rain (45 mV lower after the rain) in an acid peat (SIK 83).

There is probably little mass redistribution of inorganic solutes in humified peat, due to the low hydraulic conductivity. What may occur is diffusion. For phosphate a diffusivity of $10^{-10} \text{ m}^2/\text{s}$ has been recorded. For cations no data are available, but the high cation exchange capacity of peat indicates a low diffusivity.

Transport data for cations show that the transport may not be interpreted as a pure diffusion process in all cases. If diffusion is at all important there must be other processes superimposed. The valence state also influences the release.

The inorganic constituents of the upper 20 cm of the peat may also be relocated as a result of the absorption of solutes by plant roots. Most species cycle in the top 20 cm of the peat, but there are species with deeper roots such as the bog species *Eriophorum* (60 cm) and the fen plants *Cladium mariscus* and *Calamagrostis* spp. and the largest species of *Carex* Spp. *Rubus chamaemortus* has a type of vertical root which thrusts straight down to near the water table - 10 to 60 cm deep. Reports of 180 cm deep *Rubus chamaemortus* roots exist (CLY 83).

4 TRACE METAL REACTIONS IN SEDIMENTS AND PEAT

The behaviour of trace metals in solution is dependent on a number of parameters. The interactions between solid and liquid phase, usually named sorption, are of course important to the behaviour in sediments, soils and peat. The sorption reactions are governed by a number of parameters of the liquid phase such as the content of complex formers, ionic strength and pH as well as by the chemical properties of the trace metal itself.

Since the complex formation is of major importance to the sorption reactions it is treated separately below.

4.1 Complexation

The chemical behaviour of a metal ion in water may be drastically changed by complex formation. The successive complexation of a cation may yield cationic as well as anionic and neutral complexes, all with different properties e.g. as regards sorption onto particle surfaces.

In the following the term ligand refers to any anion or neutral molecule which can be coordinated to a metal ion.

For inorganic ligands, complex formation constants are quite well known for most metals and standard literature summarizing these is available, e.g. Sillén et al (SIL 64).

For actinides the inorganic complexes are less well known, but there is a recent review of data (ALL 82).

Similarly there are standard publications for simple organic ligands and metals.

However, humic and fulvic acids have not been so well investigated. These compounds constitute a heterogeneous group, although they may have common properties as regards complex formation. Investigations of complexation have been performed for both fulvic and humic acids with heavy metals and actinides and some general conclusions may be drawn from these.

In a study of the metal binding to organic compounds in solution in natural water from a small creek running through a forest, an oxbow lake with a bog in its catchment, and water from a raised peat bog, lead was found to be bound essentially to macromolecules in the water, while the remainder was found in free form. Manganese was mainly chelated to oligomeric organic substances, except in the acid water from the raised peat bog, where it was also found in the free state (STE 78). In a laboratory study of the interactions of copper, lead, zinc and cadmium with humic acid, the metal ions seemed to be concentrated to the fractions with large molecular sizes (>3.1 nm) (GUY 76).

The binding of metals to humic acid seems to occur at binding sites of different strength. Guy et al (GUY 76) have found two types of sites with a difference in stability constant of about 10. They also conclude that divalent metal ions may be complexed by salicylic type groups in humic acid. In a study of the complexation of zinc by humic acid, three different types of binding sites have been observed (RAN 65). One of these gave very stable complexes but the

capacity was very low - only 1 % of the total sorption capacity.

For fulvic acid Schnitzer et al (SCH 81) concludes that in the formation of soluble and insoluble metal-fulvic acid complexes, probably chelation, adsorption, and coprecipitation probably occur simultaneously. The type of interaction will depend on the specific metal ion as well as on the pH of the system.

Fulvic acid has been found to form mononuclear (1:1) complexes at an ionic strength of 0.1 between pH 3 and 5 with the following metal ions: Cu^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} , Mn^{2+} , Zn^{2+} , Ca^{2+} and Mg^{2+} . At the same ionic strength but at pH 1.70 and 2.35 respectively, fulvic acid also formed 1:1 complexes with Fe^{3+} and Al^{3+} (SCH 70).

The stability constants of some heavy metals have been found to vary in the order $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$ and for the ligands investigated $\text{EDTA} > \text{humic acid} > \text{tannic acid}$ (GUY 76). In another investigation of humic acid the order for some metals was $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+}$ (RAN 65). The order of stability of some fulvic acid complexes has been investigated. At low pH it was:
 $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} = \text{Ca}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$
 (SCH 70).

In an investigation of water soluble fulvic acid, the order of formation of insoluble metal complexes at pH 6 was $\text{Fe} = \text{Cr} = \text{Al} > \text{Pb} = \text{Cu} > \text{Hg} > \text{Zn} = \text{Ni} = \text{Co} = \text{Cd} = \text{Mn}$. A correlation with valence, 1st hydrolysis constant and effective hydrated ionic diameter of the metal ions was observed. At high fulvic acid/metal ratios (weight ratio > 2) the formation of water soluble fulvic acid complexes was favoured, while insoluble complexes were formed

at lower ratios. High fulvic acid concentrations seem to inhibit the formation of metal hydroxides (SCH 81).

Studies of the complexation of Eu(III) and Am(III) indicate that trivalent actinides form strong complexes with humic acids. Strong complexes have also been observed for Th(IV) with both humic and fulvic acid. Studies of the interaction of U(IV) and U(VI) with humic and fulvic acid have indicated the existence of two different types of binding sites. Strong binding to humic substances in nature has been reported for Th(IV), Am (III) and plutonium. The actinide humic interactions have been reviewed by Olofsson et al. (OLO 83) and will not be discussed in more detail here. Reported stability constants for some metals are listed in Tables 6 and 7.

The complexation with humic substances is strongly dependent on pH. The stability constants increase for many metals up to a certain pH e.g. for zinc and humic acid the maximum is at pH 8.5 (RAN 65:2). The competition with hydrolysis and carbonate complexation becomes significant at high pH values for many metals, e.g. for the actinides (OLO 83). At high concentrations of fulvic acid, the solubility of metal fulvic acid complexes was not pH dependent, as it was for low concentrations (SCH 81).

The value of the stability constant decreases with increasing ionic strength (SCH 70), cf. Figure 8.

The interactions of humic compounds with metals may be influenced not only by equilibrium reactions but also by reaction kinetics, since

the breaking of metal humate bonds has been observed to be very slow in some cases (OLO 83).

Figure 8. Effect of ionic strength (μ) on $\log K$ values of metal-FA complexes at pH 3.0. Acc.to Schnitzer and Hansen (SCH 70)

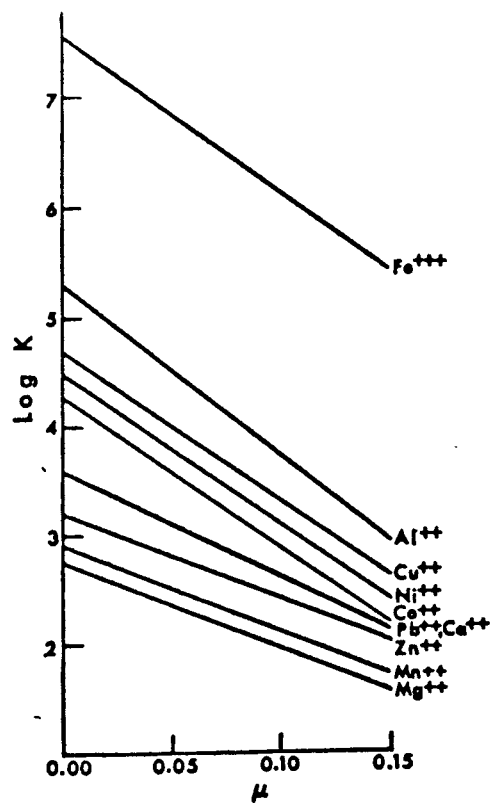


Table 6. log K for some metal fulvic acid complexes.

| Me | pH | FA/Me | logK | μ | Ref |
|------------------|-----|-------|------|-------|-------|
| Cu ²⁺ | 3.0 | 1.0 | 3.3 | 0.1 | SCH70 |
| Cu ²⁺ | 5.0 | 1.0 | 4.0 | 0.1 | " |
| Cu ²⁺ | 3.0 | | 4.7 | 0 | " |
| Ni ²⁺ | 3.0 | | 4.5 | 0 | " |
| Co ²⁺ | 3.0 | | 4.3 | 0 | " |
| Pb ²⁺ | 3.0 | | 3.6 | 0 | " |
| Ca ²⁺ | 3.0 | | 3.6 | 0 | " |
| Zn ²⁺ | 3.0 | | 3.2 | 0 | " |
| Mn ²⁺ | 3.0 | | 2.9 | 0 | " |
| Mg ²⁺ | 3.0 | | 2.7 | 0 | " |
| Fe ³⁺ | 1.7 | | 7.6 | 0 | " |
| Al ³⁺ | 2.9 | | 5.3 | 0 | " |
| Fe ³⁺ | 1.7 | | 5.4 | 0.15 | " |
| Al ³⁺ | 2.4 | | 2.9 | 0.15 | " |

Table 7. Stability constants for some metal-fulvic acid (FA), humic acid (HA) and tannic acid (TA) complexes.

| Me | K_1 | Compl | Ref | |
|--------------------|-----------------------|-----------|-------|---------------------------|
| Eu | 8×10^6 | FA | BER22 | |
| Am | 18×10^6 | HA | " | |
| Eu | 60×10^6 | HA | " | |
| Th | $10^{10.6-10^{13.1}}$ | HA (lake) | NAS80 | |
| U(VI) | 5.4×10^6 | HA | LI80 | strong site |
| " | 5.3×10^4 | HA | " | weak site |
| U(VI) | 2.7×10^7 | FA | " | |
| " | 3.6×10^5 | FA | " | |
| U(VI) | 2.3×10^6 | FA | " | |
| " | 9.2×10^4 | TA | " | |
| U(IV) | 9.5×10^6 | HA | " | |
| " | 3.2×10^4 | HA | " | |
| U(IV) | 4.4×10^6 | FA | " | |
| " | 8.8×10^4 | FA | " | |
| U(IV) | 8.5×10^6 | TA | " | |
| " | 1.1×10^5 | TA | " | |
| Cu | 1.6×10^6 | HA | GUY76 | strong kg/m^3 HA |
| " | 1.2×10^5 | HA | " | weak |
| Cd | 1.1×10^5 | HA | " | |
| Zn | 1.0×10^5 | HA | " | |
| Pb | 3.4×10^6 | HA | " | |
| " | 2.0×10^5 | HA | " | |
| Cu | 2.2×10^5 | TA | " | |
| Pb | 2.4×10^5 | TA | " | |
| Zn | 1.8×10^4 | TA | " | |
| Cd | 1.8×10^4 | TA | " | |
| Eu(III) | $10^{7.28}$ | HA | CHO80 | |
| Am(III) | $10^{3.26}$ | HA | " | |
| Th(IV) | $10^{11.1-10^{13.2}}$ | HA | " | |
| UO_2^{2+} | $10^{3.28}$ | HA | " | |
| Cu(II) | $10^{5.6-6.3}$ | FA | SAA | strong |
| | $10^{3.8-4.1}$ | FA | " | weak |
| Cd(II) | $10^3-10^{4.4}$ | FA | " | |

4.2 Sorption reactions

The sorption of cations on solid materials may be of major importance in the transport of metal ions in geological media. Since the predominant surface charge of solids in water solutions is negative, the sorption of anions is generally much lower.

In sorption reactions a number of different mechanisms for the interaction of ions in solution with the solid surfaces are included, such as ion exchange, physical sorption, chemisorption etc. See (AND 83), where an overview of the interactions occurring in water/mineral systems is given. The interactions at minerals and rocks with some fission products has also been reviewed in a KBS report (AND 83:2), and some conclusions from this may be quoted:

For cobalt and nickel the sorption is related to hydrolysis. High sorption is observed at a pH where hydrolysis becomes important and the sorption is high as long as cationic hydrolysis products are formed. When the pH is increased, neutral or negatively charged hydrolysis products may be formed and the sorption decreases.

For these reactions nuclide concentration CEC (cation exchange capacity) and temperature are of minor importance.

For strontium hydrolysis is of no importance at the normal pH of groundwater, but in groundwater above pH 9 carbonate complexation may occur. For most minerals, the sorption is low, usually with a pronounced pH dependence. Other important parameters are ionic strength and CEC. A

nonselective sorption due to electrostatic interactions between negatively charged mineral surfaces and Sr^{2+} seems to occur.

For cesium no hydrolysis may be expected and pH has less importance than for Sr. For most minerals, however, the sorption of Cs is higher than for Sr. Important parameters are nuclide concentration and ionic strength. A selectivity for Cs-sorption is found for some minerals, mostly sheet-silicates.

For technetium sorption is due to a reduction of TcO_4^- to $\text{TcO}_2(\text{s})$ and as anions are poorly sorbed, the sorption is dependent on the redox potential.

Iodine is also anionic and poorly sorbed. Minerals containing ions capable of forming iodides with low solubility (Ag, Mg, Pb etc) do, however, sorb I^- .

For actinides the sorption reactions have been summarized by Allard (ALL 83).

The experimental observations on the sorption behaviour of actinides on geological material, for Am, Np, Pu, Th, Pa and U can be summarized qualitatively as follows:

- For all systems the sorption is drastically increased when hydrolysis starts. Sorption maxima are generally obtained in the pH-range where neutral hydroxy complexes would dominate in solution.
- A decrease in sorption at high pH seems to coincide with the formation of anionic species (e.g. with OH^- or CO_3^{2-}).
- In the pH-range where hydrolyzed products dominate in solution the sorption is less affected by the cation

exchange capacity of the solid sorbent than in non-hydrolyzed systems.

- The sorption is fairly independent of the ionic strength for actinides in their lower oxidation states in the pH-range where hydrolysis dominates. For unhydrolyzed systems the sorption decreases with increasing ionic strength.
- The sorption of hydrolyzed species increases slowly with time. The time to reach equilibrium decreases with increasing ionic strength and/or increasing temperature.
- The formation of colloidal fractions e.g. of clayish materials, that would lead to lower apparent distribution coefficients, decreases with increasing ionic strength.
- The sorption actinides in the lower oxidation states (III, IV) are fairly independent of the nuclide concentration (for total concentrations well below the solubility product of any sparingly soluble compound). For the higher oxidation states, in cases when polynuclear anionic species can be formed (e.g. An(VI)-CO₃²⁻), a drastic reduction of the sorption with increasing nuclide concentration (or concentration of e.g. CO₃²⁻) can be obtained.
- The presence of organic complexes can lead to a reduced sorption.

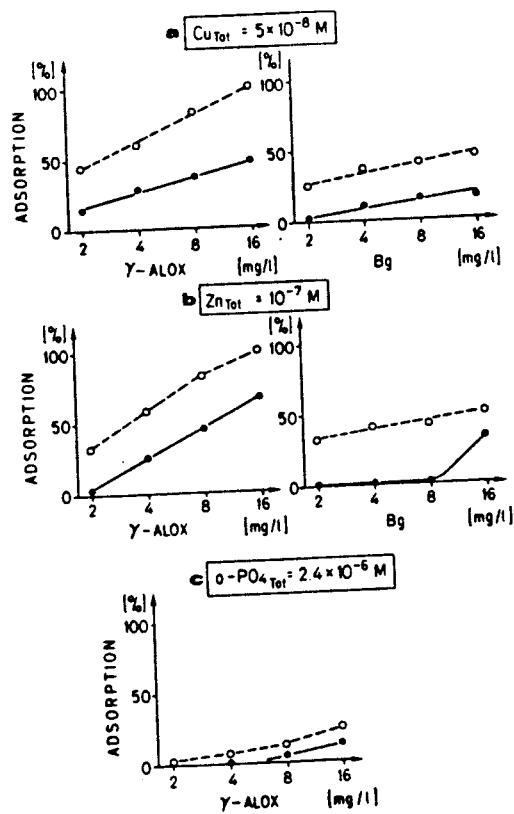
Note should also be taken of the changes in sorption behaviour which would occur if the oxidation state were varied, e.g. from III or IV, which subsequently could be highly hydrolyzed in the environmental pH-range, to V with a low degree of hydrolysis, or VI to form strong anionic carbonate complexes.

It is however very important to note that in all these investigations the influence of organic complex formers has not been considered. This may lead to complexes of different charges and properties.

Sorption may also occur on solid organic substances.

Dissolved organic matter may lead to a lower adsorption of metal ions on mineral surfaces due to an adsorption of organics on the solid. This has been shown for the sorption of copper and zinc on $\gamma\text{-Al}_2\text{O}_3$ and lake sediments, cf. Figure 9 (BAC 82).

Figure 9. Cu, Zn and phosphate adsorption as a function of particle concentration and natural organic matter. O---O without organic matter, ●—● with 2 mg DOC/l. Acc. to Baccini et al (BAC 82)



In an investigation of the sorption of metal ions on humic acids isolated from marine sediments, an effective sorption by chelation, cation exchange and surface adsorption has been observed. The quantities of metal ions complexed varied from 40 to 205 mg/g of organic matter. In the presence of Co, Cu, Mn, Ni and Zn humic acid and peat moss showed preferential absorption of Cu. The bonding strength was very firm because it could not be displaced by ferric iron or cation exchange reagents. Peat moss was found to absorb significant quantities of various metal ions (RAS 74). Unfortunately all studies were performed with constant concentration (200 ppm) of the metal ion and the result was only given as mg sorbed/kg solid, not in terms of K_d or sorption isotherms.

By developing a simple equilibrium model for the adsorption of trace metals based on the linear portion of adsorption isotherms, it has been shown that trace metal partitioning can potentially be predicted from laboratory studies with the use of conditional equilibrium adsorption constants. The constants determined for Cu and Cd adsorption on bentonite clay, $\text{Fe}(\text{OH})_3$, MnO_2 and humic acid in seawater show that this model is applicable for trace metal concentrations existing in the natural environment. The constants determined for Cu were much higher than those for Cd for all solids. The affinity of humic acid relative to the other phases was high for Cu and low for Cd. On the basis of the laboratory results, the model predicts that the clay fraction will be a major sink for Cu and Cd in the artificial phases used (OAK 81).

The sorption isotherms for Cu and Cd in seawater on humic acid are linear over a larger concentration range than observed for bentonite, $\text{Fe}(\text{OH})_3$ or MnO_2 , cf. Figures 10 and 11. The distribution of the metals between the different solid phases is given for various concentrations of clay. For Cu the humic acid is responsible for a large part of the sorption capacity, while for Cd the clay is more important. As might be expected for a hydrolyzing metal, the sorption increases with pH for Cu in the range where hydrolysis becomes important. An almost total sorption occurs below pH 8. The copper sorption on bentonite is not especially dependent on the salinity of the water phase - a fact that might be expected from the hydrolytic behaviour of Cu.

In Table 8 the distribution coefficients for Cu and Cd on the various solids used are given. The sorption is high - the unit l/g equals m^3/kg , and Cu is thus almost completely sorbed (OAK 81).

Table 8. Distribution coefficients for Cu and Cd in seawater. Acc. to Oakley et al (OAK 81).

| solid phase | Cu | | Cd | |
|--------------------------|----------------|-------|----------------|-------|
| | K_{AD} , L/g | R^2 | K_{AD} , L/g | R^2 |
| bentonite clay | 43 | 0.97 | 1.1 | 0.90 |
| $\text{Fe}(\text{OH})_3$ | 205 | 0.86 | 4.4 | 0.98 |
| MnO_2 | 7339 | 0.95 | 15.0 | 0.96 |
| humic acid | 366 | 0.98 | 0.2 | 0.99 |

* pH 8.0; S = 32‰; T = 20 °C.

Figure 10. Adsorption isotherms for Cu in seawater. Acc. to Oakley et al (OAK 81)

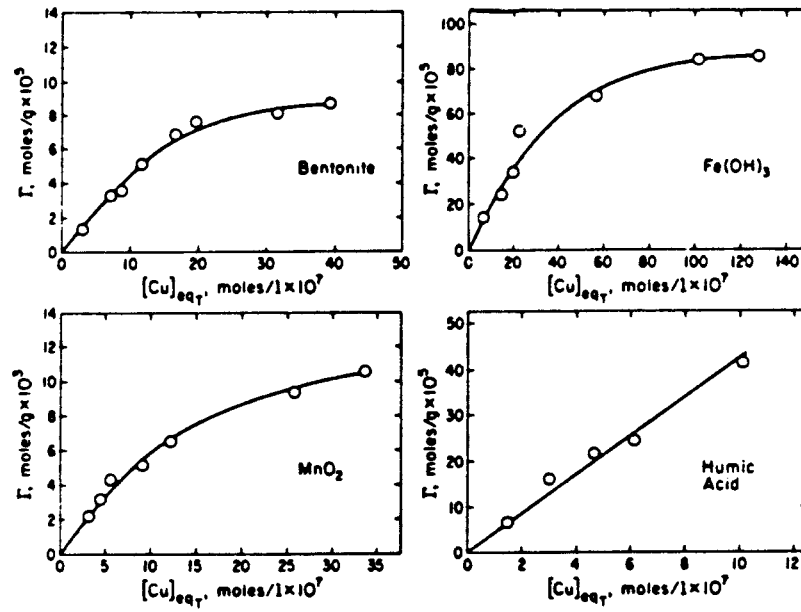
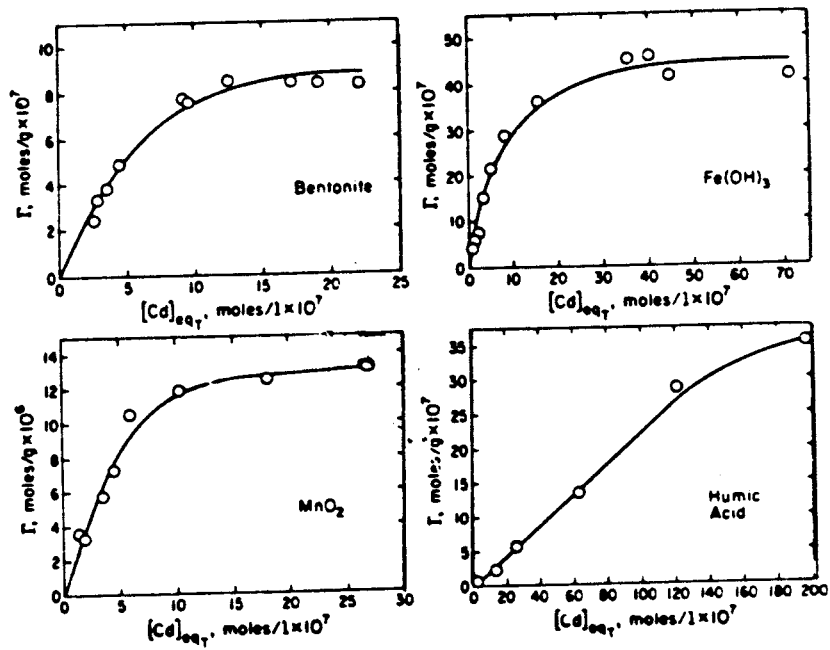


Figure 11. Adsorption isotherms for Cd in seawater. Acc to Oakley et al (OAK 81)



5 TRACE METALS IN PEAT - ANALOGIES

The content of mobile forms of microelements in peat depends on the pH of the peat as well as its degree of decomposition. A high migration ability of zinc and manganese in peat deposits has been established. In general lowmoor peat deposits (pH 7-8) contain the greatest concentrations of microelements as compared with highmoor deposits (pH 3.5-4), with the exception of some elements such as zinc and others. Some kinds of peat possess the selective ability to concentrate certain microelements several times more than background contents. For example highmoor *Schezeria sphagnum* peat accumulates copper and zinc much more than other kinds of peat; manganese is accumulated in *Sphagnum* peats kinds of the highmoor type; lowmoor woody peat contains several times as much cobalt and molybdenum as other kinds of peat. Plants of eutrophic type are much more enriched in microelements. Concentration increases are observed in boundary zones adjacent to the point where feed water flows in. Two maxima of the contents are generally encountered: in the root layer and in the ground horizon. (Studied elements: V, Cr, Co, Ni, Cu, Be, Ga, Mo, Pb, Zr, Y, La) (LAR 72).

The contents of trace elements in Northern Ontario peat have been analyzed at 0-20 cm and 20-40 cm for Pb, Cu, Cr, Cd and Zn. Only in the case of Pb were differences observed between different peat types and depths (GLO 82).

In a study of the mobility of ^{226}Ra in soils, a strong fixation of Ra released 30 years ago has been observed in a strongly podzolic gley soil. Simple organic acids seem to increase the mobility. There is a direct correlation between

the ^{226}Ra content and humus, exchangeable bases and pH in the root zone (TAS 78).

Uranium escapes from the lithosphere in the form of mobile carbonate complexes. Humic acids may complex the uranium and solid humic compounds give a fixation of uranium. In a study of 14 arbitrarily chosen peat bogs in different parts of Finland, the uranium concentration was found to have a sharp peak at a level about one fourth from the bottom of the bog. Lead accumulates both at the surface and at the same level as uranium, cf. Figure 12. The accumulation of lead at the surface is attributed to the influence of living plants, while a complexation with humus may explain the accumulation of both uranium and lead at greater depths. Nickel is not enriched by living plants and the complexation with humus is also less than for the other metals (ERÄ 69).

Uranium is often found in coal strata, and the enrichment of U in coal has been demonstrated in laboratory experiments (M0054). Lignite, peat and other similar decayed fossil plant debris adsorb uranium quickly from a very dilute aqueous solution in the pH range of 3-7. A very steep sorption isotherm has been observed (Langmuir isotherm). At trace concentrations the enrichment factor (distribution coefficient) is 10 000 ml/g ($10^3 \text{ m}^3/\text{kg}$). The initial concentrations used in these experiments correspond to those commonly found in nature. Saturation of peat occurs when the content is about 10 %. The investigators have showed that the sorption is reversible. For thorium similar sorption isotherms have been reported, with enrichment factors of 30 000 ml/g ($30 \text{ m}^3/\text{kg}$). At pHs below 3 the U can be easily desorbed, while fixation occurs between pH 3 and 7. It has also been shown that the enrichment

constant increases very strongly with the valency and with the atomic weight of the cation. UO_2^{2+} and Th^{4+} cations and the ions of rare earth metals are adsorbed on to peat to an extremely large extent, because their valencies and atomic weights are high. The various cations compete with each other and with those of higher valency and atomic weight and expel others of lower atomic weights and valency. If the humic acid is extracted from peat by NaOH the peat loses the major part of its U fixing capacity while the resulting humic acid, liberated by acid, still has the U sorbing capacity.

The author claims that the fixation by means of cation exchange on to humus is responsible for the enrichment process which concentrates the uranium in a proportion of about 1:10 000 in fossil plant debris and bioliths (SZA 58).

Uranium is considerably more mobile than radium in surface waters containing small amounts of calcium bicarbonate. Radium is readily sorbed by clays as well as by peat. In peat, uranium is bound to the humic and fulvic acids soluble in alkali, whereas the radium is associated with the insoluble residue. Under oxidizing conditions the elements appear to be retained by ion exchange but in the presence of high concentrations of calcium in the water, the radium in the peat and in the insoluble residue becomes nearly unexchangeable. The exchangeability of the radium bound to the humic acid is however retained. These studies have been performed in the taiga permafrost areas. Batch sorption experiments showed an increased uptake of radium by peat when pH increases from 5 to 8, while the uptake of uranium was highest at pH 6, cf. Figure 13. Distribution coefficients are not given in the

paper, but these are said to vary greatly with the kind of peat. Desorption experiments showed that much of the uranium could be eluted from the peat, while radium was less easily desorbed. For radium the influence of calcium on the desorption properties was evident; thus the desorption was much less if the sample was pretreated with Ca-solution. The table also gives a comparison of the sorption on some substances found in peat: humic acid, humins, floodplain loam, and pure kaolinite. The sorption of radium on peat is similar to that on humins, indicating that radium is bound to the humin fraction. The mobility of uranium observed in the laboratory experiments is not related to the observed enrichment of U in peat deposits. A stronger binding of U(IV) than U(VI) may be involved since there is a possibility of reduction of the U in peat (TIT 67).

Lower plants (mosses, algae and microorganisms) accumulate more uranium than higher plants. Accumulation of uranium by living plants plays an unimportant role in its concentration in peat. A study of the uranium content in plants, peat water and soil in eastern Siberia has been performed in areas where the U content of the water ranged from 1.5 to 2.3 ppb. Little difference was found in the U contents of soil samples taken at the surface and at 0.5 m depth. Mosses were shown to accumulate large amounts of U and there were correspondingly high concentrations in peat (LOP 70).

Figure 12. Ni, Pb, U, and ash contents and pH-values in a peat bog. Acc to Erämätsä et al (ERÄ 69)

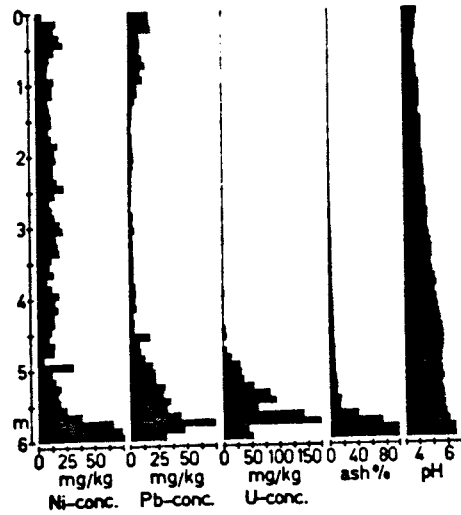
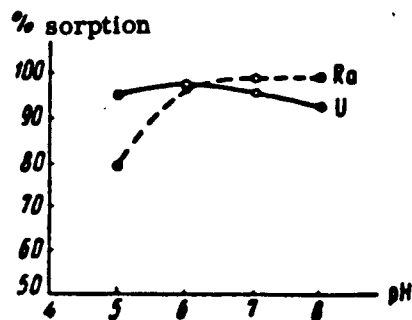


Figure 13. Effect of pH on the sorption of U and Ra in peat. Acc. to Titayeva (TIT 67)



6 CONCLUSIONS

In the evolution of a lake or a Baltic bay into farming land or peatland a wide range of possible chemical conditions may be expected to occur within bottom sediments and in the peat.

There are some parameters in the interstitial water which are of major importance to the behaviour of trace metal ions. The most important of these seem to be pH, Eh, ionic strength and content of complex formers.

pH may vary from 3.5 to over 8. The low values are most likely to occur in peat and in acid soils, while pH values of 7 to 8 are the most common in sediments. In some types of peat pH values up to 7 may also occur. Since the possible sorption of cations usually increases with pH, especially for easily hydrolyzed ions, the systems with high pH may be expected to exhibit a lower mobility of trace cations.

The absolute value of the redox potential, Eh, is a quantity that is difficult (or impossible) to determine. A significant difference between oxic and anoxic conditions may nevertheless be observed. In sediments Eh changes may occur over the year, especially in the surface layer due to variations in the aeration and oxygen consumption of the overlaying lake water. Deep sediments and peats also tend to be depleted of oxygen. The behaviour of redox sensitive metals (e.g. Tc, U, Pu) may be determined by the redox conditions to a very large degree, while for others there is one predominant valence state and the redox conditions will only be of importance if they influence the properties of the solid or water chemistry.

The ionic strength also varies over a wide range for the water types in question. The amount of dissolved ions may be from some mg/l up to 16 000 mg/l. This means that the sorption may vary very much for uncomplexed cations depending on the type of water. The complexation is also dependent on the ionic strength (stability constants decrease with increasing ionic strength).

In all the water types discussed, the content of potential complex formers may be quite high. Among these there are both inorganic species like phosphate, carbonate and sulphate and organic compounds (humic substances). The influence of complex formers may be due to several mechanisms. They form complexes with trace metals that may be both more and less soluble than the uncomplexed ion. The complexes may also be sorbed to a greater or lesser degree than the uncomplexed ion. There may also be a sorption of organic complexants on the mineral surfaces that inhibits sorption of metal ions. Complexation may occur with both macro and trace components and competition has thus also to be considered.

Complexation may occur with solid organic substances. This may in some cases be virtually irreversible.

The properties of the solid mineral phases present are also of great importance to the behaviour of trace metals. Metal ions may be sorbed on the surfaces, causing both reversible and irreversible incorporation into the solid phase. The interstitial water composition is also influenced by the solid phases. The interactions may however be slow, and equilibrium conditions cannot always be expected.

Some general conclusions on the behaviour of trace metals in peat may be drawn from investigations of metal enrichment in nature. Observations have been made on the difference in the occurrence of uranium and lead in peat deposits. Conclusions about the plant availability have also been drawn from this type of investigations. The investigation show enrichments of uranium and lead in the bottom layers of peat, while lead is also enriched on the surface.

Radium seems to be more strongly bound to the organic solids than is uranium, and here the competition with calcium is important.

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Anne-Britt Wilkens

HUMAN IMPACT DURING THE EVOLUTION
OF A LAKE OR A BAY

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1 INTRODUCTION

Man's basic relationship to the environment has always been founded on the uses he can make of various components for food, shelter etc. At the same time he himself is a part of the ecosystem, and he has many opportunities to change the system so as to fit his needs.

If a lake or a bay is assumed to have been polluted by some metal ions, for instance, and this pollution is assumed to be bound in the sediments or lake biota, which ways can this pollutant be released to the environment during and after the terrestrialization of the lake? How can human impact influence the release and recycling of the element?

It is almost impossible to predict all the ways in which man may in the future utilize a lake or bay area and its resources during all stages of development.

Consequently in this paper different methods that have been applied especially during the 20th century are discussed, and mention is also made of some aspects of applications which are directed towards energy conservation that may be relevant in the near future. It is not possible to deal with all the probable consequences, but some of the more important effects are treated.

A great deal of the arable land in Sweden has once been at the bottom of lakes or seas. During the 19th century the increasing population necessitated the reclamation and cultivation of bog areas and major drainage projects.

Nevertheless, more than 20 % of the Swedish land area is nowadays classified as wetlands, and this constitutes a potential resource for both food and energy production, see figure 1.

The eutrophication rate of a lake may be counteracted or accelerated as a result of human impact. On one hand, some of the most eutrophicated lakes have been restored by chemical precipitation and sedimentation, for instance Trummen near Växjö, and in connection with aquaculture the water has to meet certain demands as to quality claims. On the other side it is well known that man accelerates the eutrophication rate as a result of the fertilization of arable and forest soils clear-felling within the catchment area, or the discharge of waste water from industries or households.

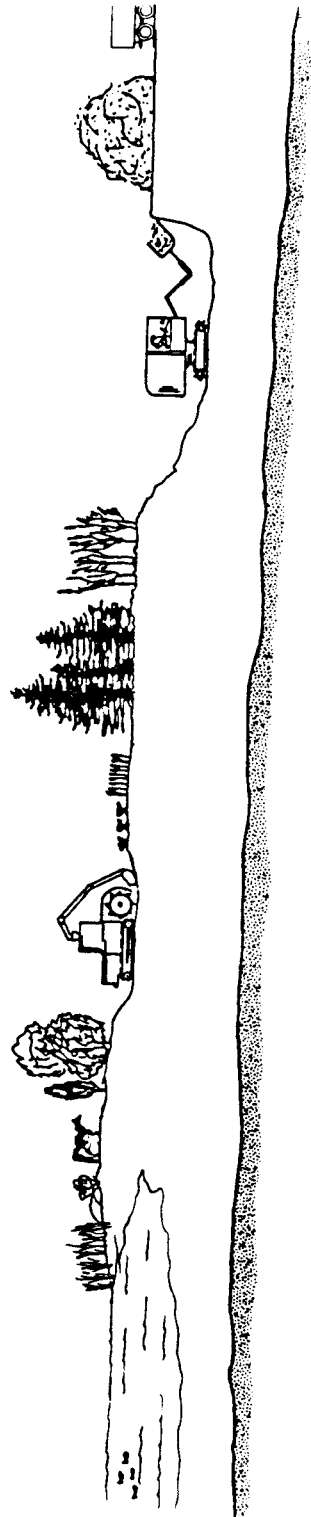


Figure 1. Human impact during the development of a lake. After /28/

2 DIRECT IMPACT

This paper draws a distinction between direct or intentional impact, and indirect impact.

Indirect impact refers to involuntarily attained effects, usually with a negative influence on the environment, such as acidification and leaching.

2.1 Exploitation of the area

During its development from open water to solid ground the area passes through stages when it can be classified as wetland.

The major categories of wetlands according to Swedish conditions are listed as follows:

- mires (peatlands)
- littoral wetlands
- moist or wet areas without peat formation /17/

The interest in utilization of our wetlands has increased considerably during the last decade, and this utilization may have lasting consequences. Hydrology, water chemistry, vegetation and fauna will be affected.

In this paper, the exploitation of an area is assumed to include three main activities: drainage, agriculture and forestry. Drainage is assumed to be a prerequisite for the other two.

The use of wetlands for recreational purposes is a possible application which is not discussed in this paper.

2.1.1 Drainage

The most radical impact on a lake may be assumed to be produced by draining it.

During the second half of the 19th century a great period of drainage and reclamation ventures began in Sweden. Many lakes were drained dry in order to get new arable soils.

For the exploitation of wetlands, sedimented areas or peat soils drainage is the primary procedure.

A requirement for the effective utilization of soils with imperfect or poor natural drainage is the removal of excess soil moisture.

In /23/ it is stated that water moves faster laterally than vertically in poorly humified peat but that the difference in more humified peat is insignificant. Poorly humified sphagnum peat showed the greatest transmission rates.

Two factors are of special importance:

- the water transmission of the peat
- the root penetration power in different types of peat.

The objective is to lower the moisture content in the upper layers of the soil, permitting oxygen penetration to the root zone and diffusion of carbon dioxide from the roots.

Surprisingly, even irrigated soils often require an extensive drainage system.

It is well known that the drying of fresh peat is attended by shrinkage and that neither the original water content nor the original peat volume is regained, when the dry peat is brought into contact with water again /12/. To a certain extent the shrinkage is reversible. Consequently it is found that the total shrinkage on drying may amount to 80 vol % whereas the reswelling of a decomposed peat may be limited to 10 % of the original volume. As shrinkage is generally greater the more the peat is decomposed it follows that this property is particularly one of humified matter. See figure 2.

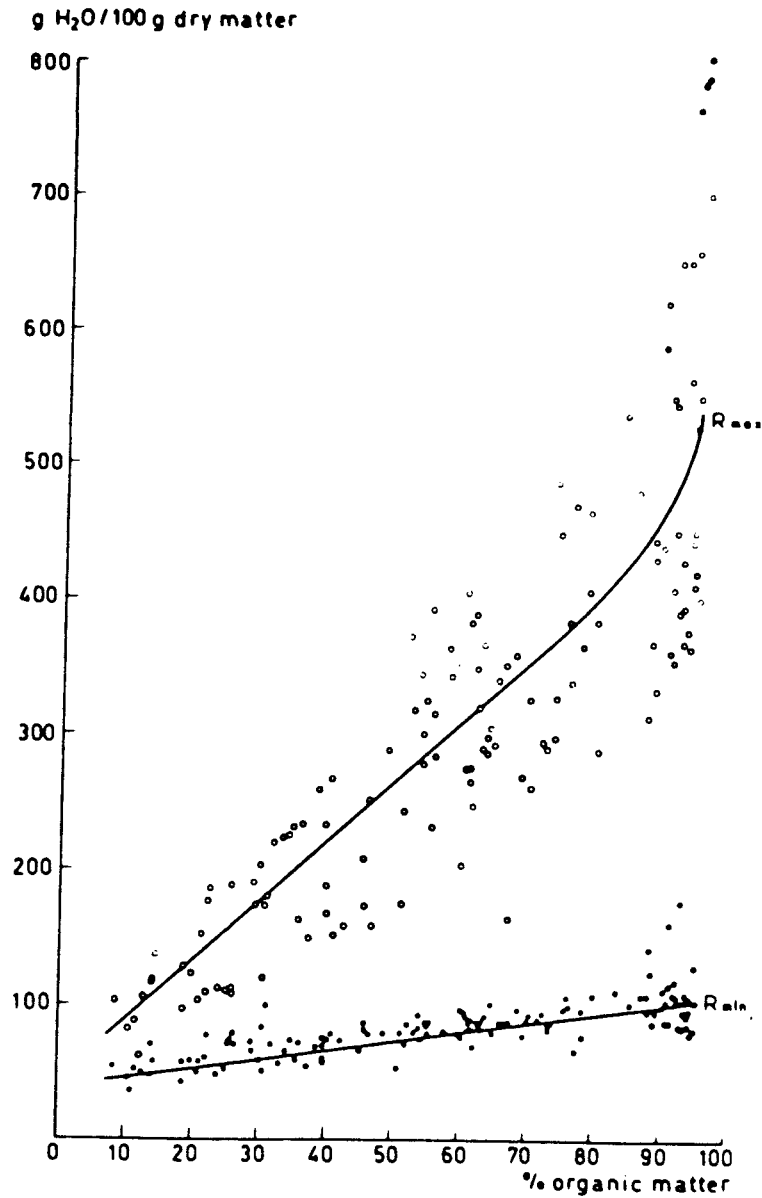


Figure 2. "Centrifuge moisture equivalents" (remaining water content after centrifugation at 1000xg) of fresh peat (R_{\max}) and of peat which has been dried, ground, and resaturated with water (R_{\min}), as a function of organic matter content. From /12/.

2.1.2 Agriculture including the nature of -----organic soils-----

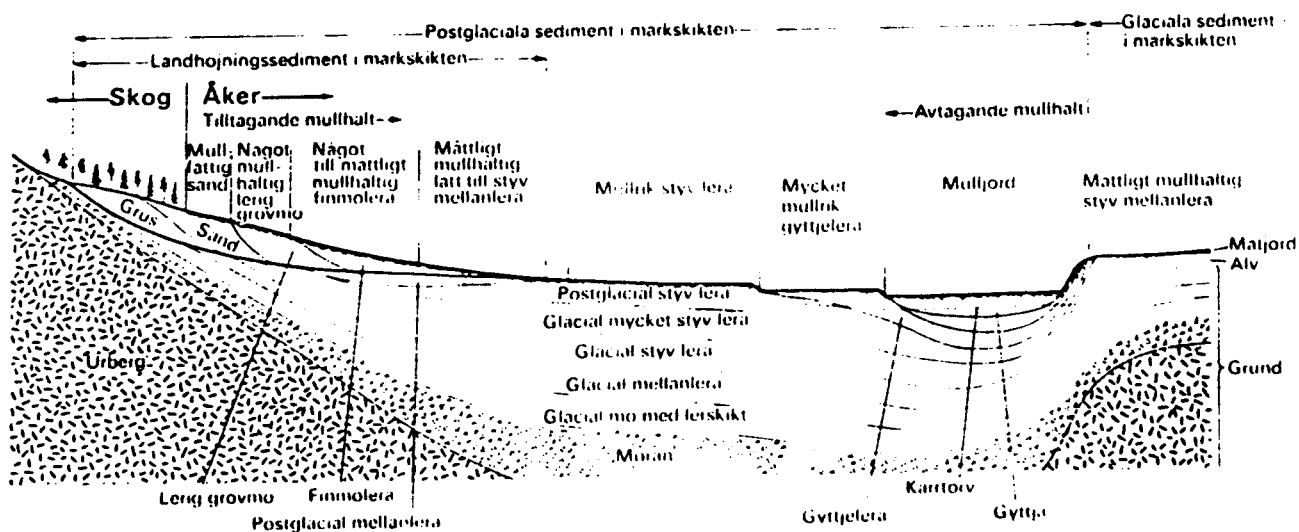
Arable soils are discussed in detail in agricultural and soil literature /5, 8, 18/. On the basis of organic content, two general groups of

soil are recognized, mineral and organic. Soils with more than 40 % organic matter are classified as organic or Histosols /14/. Our knowledge of organic soils is still incomplete, for instance as regards the particle size distribution.

Organic soils are produced by biotic and abiotic factors. They can be divided into two groups, sedentic or autoctonic and sedimentic. Peat soil belongs to the first group but gyttja and dy belong to the second.

The growth of peat is described in a separate paper by Karin Andersson, 1984. Gyttja is formed in lakes or bays of more or less decomposed plants and animals ("ävja") mixed up with clay minerals. Dy is a light black-brown earth formed by chemical precipitation in oligotrophic lakes. The figure below illustrates the stratification of different sediments in a Swedish valley.

Figure 3. Vertical section showing the stratification of a typical valley in Sweden /34/



Organic matter accumulates wherever the net rate of photosynthesis exceeds the rate of oxidation of organic matter. The oxidation of organic matter may be reduced or limited by several factors, such as low temperature, the absence of mineral nutrients, lack of water (under aerobic conditions) or the lack of oxygen (under anaerobic conditions).

As illustrated in the foregoing figure most soils, with the exception of blocky moraine, can have potential interest as arable soils.

It must, however, be noted that organic and mineral soils differ considerably from both a chemical and a physical point of view.

For example, peat soils have a lower bulk density than mineral soils and in /23/ the following average values of bulk density were recorded.

| Soil | Bulk density kg m^{-3} |
|-----------------------|---------------------------------|
| gyttja | 375 |
| dy | 350 |
| bog soil (kärrjord) | 250 |
| swamp soil (mossjord) | 150 |

The low density of an organic soil is a disadvantage in connection with cultivation and crop production. It gives a lower bearing capacity and in agricultural techniques today, most machines are extremely big and heavy.

The application of mineral soils to ameliorate the physical properties of peat has been tried earlier /23/.

The structure of a soil should also be considered. Intensive cultivation of some organic soils will produce a powdery structure and thus a poorer water-sorption capacity.

It should be noted that a large amount of the water content in a peat soil is colloiddally bound and not available to plants; this is illustrated in /23/ where a comparison is made between the wilting percentages of three different soils.

| <u>Soil</u> | <u>Wilting percentage</u> |
|-------------|---------------------------|
| Sand | 1.5 % |
| Sandy clay | 7.2 % |
| Peat | 33.2 % |

The colloidal nature of organic soils is more pronounced than in most mineral soils. Their surface area exceeds even that of montmorillonite clay by a factor of two to four and the cation exchange capacity is correspondingly greater. Cations are adsorbed in the same order of magnitude in organic as in mineral material:



Some important differences should be noted. The amount of adsorbed Ca is much greater in organic than in mineral soils, and a higher proportion of total, mineral cations are exchangeable in organic soils.

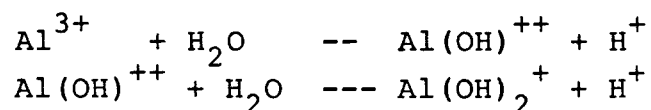
These two facts are shown in the following table.

Table 1. Cationic conditions in two woody peat soils, one low and the other high in lime /8/

| Cation | Exchangeable metallic cations meq/100 g | | Percent of cations exchangeable | |
|-----------|---|----------------|---------------------------------|----------------|
| | low lime peat | high lime peat | low lime peat | high lime peat |
| Calcium | 39.8 | 159.7 | 80 | 75 |
| Magnesium | 9.7 | 12.0 | 100 | 51 |
| Potassium | 0.87 | 1.16 | 34 | 27 |
| Sodium | 0.80 | 0.87 | - | - |

All this is in contrast with a mineral soil, where usually less than 35 % of the calcium, less than 10 % of the magnesium and less than one (1) % of the total potassium are exchangeable.

Hydrogen and aluminium tend to dominate acid soils. Both contribute to the concentration of H^+ ions in the soil solution, adsorbed hydrogen directly and aluminium indirectly through hydrolysis, as follows:



Most of the other cations, exchangeable bases, neutralize soil acidity. The proportion of the cation exchange capacity occupied by these bases is called the percentage base saturation /8/. From an agricultural point of view this is an important factor.

2.1.2.1 Grazing

An initial step in the utilization a wetland area, which may not even have been drained, is by grazing.

In earlier times the drove of cattle was far more important in agriculture than it is nowadays, and the number of animals on a farm was often maximized rather than optimized, in relation to the available area. The consequence of this was that the utilization of wetlands for grazing and hay-cutting was a requirement.

Manure was a limited resource preferably used in arable fields. The grasslands became successively depleted of plant nutrients. Not until the industrial fertilizers came, could a restricted fertilization of natural grasslands start.

When covered by permanent grassland an organic soil is more slowly and altogether less oxidized than through crop cultivation. The grasslands do not need such efficient drainage as arable fields and can even withstand short periods of flooding, near rivers or streams.

In forage production it is, however, verified that a rather low ground water level gives a better quality as the poor grasses are pressed back by the better types with deeper root systems.

2.1.2.2 Crop production

The necessary steps to bring a peat bog or drained wetland under cultivation, aside from drainage, vary with the type of peat and the kind of living and dead matter that covers the area. The first step is to remove all of the coarse debris, including stumps and roots.

In some countries it is a common practice to burn off the remaining coarse material, but the

deeper layers must be sufficiently wet not to burn.

A better technique is to cultivate the soil a few times and to accelerate the oxidation of the upper soil. A newly reclaimed area is usually an unsatisfactory medium for crops. The peat bog has been under anaerobic conditions perhaps for centuries and the roots of cultivated plants do not penetrate this medium. This can be due to toxic amounts of, for instance, sulphuric acid or metal compounds but is partly dependent on the lack of oxygen.

After the initial operations it can be recommended that suitable grasses should be sown and the soil left in pasture for a couple of years.

In considering the use of peat for crop production it is well to emphasize that there is usually a great difference between raw peat and peat which has been drained and oxidized for some time. In the raw state all types of peat have a low value of nutritive constituents. When the peat is properly aerated, cultivated etc the change from peat to a material resembling humus may take place rapidly /5/.

In practically all peats the levels of elements are inadequate for crop production, and a successful conversion to productive soil depends largely on the application of balanced fertilizers. Not only the major elements are needed, but different crops require minor elements in varying degrees, and copper, molybdenum, boron, zinc and manganese appear to be important.

Lime deficiency is characteristic in most sphagnum and woody peats. The pH values in these peats commonly lie between 3.0 and 5.0.

Deficiencies in minor elements deficiencies are common in cultivated peats or mucks, but properly managed peat soils can be most productive.

After a few years under grass almost all crops can be cultivated in this type of area. Especially good results have been obtained with onions, cabbages, beans and potatoes.

2.1.3 Forestry

In these days the most extensive demands on wetlands come from forestry. In Sweden these claims have been quantified to 1.5 million hectares.

Around 7 million hectares of Swedish peat soils have today none or little forest production, but a great deal of this area will presumably become productive in the future, above all as a result of drainage techniques, which in recent times have been greatly developed. However, the drainage must be supplemented by a nutrient analysis of the peat, especially as regards potassium and phosphorus down to the depth where the roots of the trees mostly stop.

2.1.3.1 Traditional forest culture

Recent plans for increasing wood production in Sweden aim at increased drainage operations, but the nutritional status of the peats often becomes a delimiting factor.

Forestry differs from agriculture in that the rotational time for the crop is much longer, and forest plantation does not decrease the organic peat layer as quickly or to the same extent as in agriculture.

Forestry today include among other things clear felling, fertilization, and treatment with chemical biocides. Clear felling especially when accompanied by burning, quickly solubilizes the nutrients and an increased eutrophication rate in recipient water is a risk, see also the chapter on leaching, 3.2.

Wood from traditional forest culture can be utilized in many ways, as a building material for instance or as biomass and fuel.

2.1.3.2 Energy forest

The cultivation of energy forest entails the plantation of fast growing trees in order to produce raw material for energy production.

Usually one can distinguish between intensive and extensive cultivation. The term intensive forest cultivation refers to planting with a quick crop rotation, 1 to 5 years, using different *Salix* species /13/. The plants are fertilized according to the growth capacity and if necessary the plants are also irrigated. Harvesting is carried out with specially designed machines. New generations are ensured since shoots grow out from the stumps, and these have been calculated to have a life span of 20-30 years.

The extensive cultivation of energy forest utilizes species such as poplar, aspen and

birch. These are suitable for a slower crop production over 15-20 years. The cuttings are planted out more sparsely and even thinned out if necessary. Fertilization is carried out at the same time as planting and thereafter at intervals of several years. Felling of the mature trees is planned using existing techniques.

Extensive forest cultivation does not make such demands on ground preparation and drainage as intensive energy forest.

The expected annual production is calculated to be 20 tons (DM) per hectare on farm land and 15 tons per hectare on wetlands. In /13/ wetland areas totalling 2.1 million hectares are thought to be suitable for energy forest, i.e. nearly 50 % of the total wetland area.

The cultivation of energy forest is in its early stages; nevertheless environmental research has begun. So far this has been conducted in the following areas:

- water balance
- water quality
- flora
- fauna
- landscaping.

2.2.1 Aquaculture

The rapid development of aquaculture today can partly be explained by the increasing pollution of seas and lakes. For instance, the pH-values in water are important for the comfort of the fishes. For fish-production pH-values are recommended to lie between 6.5 and 8, and

strongly basic as well as acidified waters are classified as unfavourable /3/.

Pollutants in the water can be accumulated in the fishes either directly through the water or through polluted food.

Culture techniques are developing along low-energy cultivation lines where the nutrients are recycled /2/. Aquaculture-agriculture-industry is intended in the future to be more and more integrated, so that warm effluents and chemical waste products can be utilized for fish-production.

The environmental consequences of cultivation of fish, mussels and algae in water bodies and coastal areas depend on many factors, e g the volume of production and the techniques used. In aquaculture the surrounding water may be loaded with phosphorus from fodder excretion products. The environmental consequences of the cultivation of fish are however estimated to be small /1/ compared with other activities. The aquaculture is often judged to be "self regulating", since negative environmental effects also damage the cultivation.

The treatment of lakes with lime is sometimes necessary to counteract the negative effects which acidification may have on aquaculture activities.

2.2.2 Reed

Large amounts of organic matter are produced by aquatic plants in marshes, in littoral zones of lakes and in brackish water areas /16/.

At present only a small portion is utilized, but as late as 25 years ago reeds were harvested as forage in our country.

The total reed-covered area is estimated to be between 50 000 and 100 000 hectares. Reeds grow on a variety of substrates, from minerogenic to organic soils and they can even grow in anaerobic soils. They are thought to extract nutrients mainly from the soil, but when exposed to nutrient-rich water they can also take up elements through the finely branched roots on the lower part of the culm /16/.

Reeds have a deeply penetrating perennial biomass, composed of rhizomes. The rhizomes have a life span of a few years.

This vegetation rarely suffers from water deficiency and as the plants often grow in nutrient rich medium, a high productivity can be expected.

Aquatic plants have for a long time been utilized as paper, building material etc. Nowadays the greatest interest is associated with the energy content. Reeds harvested in summer can be calculated to have an energy content which corresponds to more than half a litre of oil calculated as biomass m^{-2} /16/.

The use of aquatic plants and macroalgae for energy production has been discussed, for example using:

- methane fermentation
- biomass fuel and wood mixture.

Biomass (woodchips, straw and reeds) cannot be burnt as efficiently as oil. There is, however,

little variation in energy content between different plants, especially when calculated on an ash-free basis. But while algae have a high ash content, in some cases over 50 %, winter-harvested reeds have a mean-ignition residue of 4 %; this should be compared with wood having 0.1-2.0 % of the DM.

The environmental effects connected with the conversion or combustion of reeds depend to a great extent on the technology. When compared with fossil fuels biomass has the advantage of a low sulphur content, for reeds this varies between 0.1 and 0.2 %. Reeds also contain small amounts of heavy metals and for this reason the ash could possibly be returned to the reed stand to recycle nutrients /16/.

2.2.3 Peat

Active peatlands are among the few existing ecosystems which produce a long-term surplus of energy /23/. The possibilities of utilizing peat deposits for agricultural and forestry purposes are discussed in previous chapters. But peat has unique properties. It has an excellent power of adsorption and adsorbs water to about 20 times its own weight, but can also take up organic and inorganic nutrients as well as pollutants.

Undrained peatlands have also been used for experimental dumping of sludge /21/.

Presumably future research will find ways to convert peat into other macromolecular substances with diversified potentials, such as waxes and medicinal agents or, into smaller molecules such as solvents.

The most important possibilities for utilizing peat can however be summarized as follows:

- as an energy source
- as mineral soil fertilization
- as raw material.

Since peat may contain impurities which could pollute the environment when it is utilized, the first two applications will be discussed in this paper.

2.2.3.1 Peat in energy production

Since the oil crisis of 1973, energy saving and oil substitution is an important aim in the Swedish energy policy. For example, gasification studies have been performed in Sweden for more than 10 years /24/.

Peat may be regarded as a reservoir of stored solar energy which can be recovered in different ways. It must however be kept in mind that peat is a non-renewable energy source, and that the carbon dioxide emitted through burning of peat is not balanced by a similar uptake.

The peat reserves in Sweden are estimated at 4000 million tons of oil equivalents, corresponding to the total biomass production in Sweden during 100 years. Peat is a young material compared to the fossil fuels, with chemical resemblances to ignite, see figure 4 /20/.

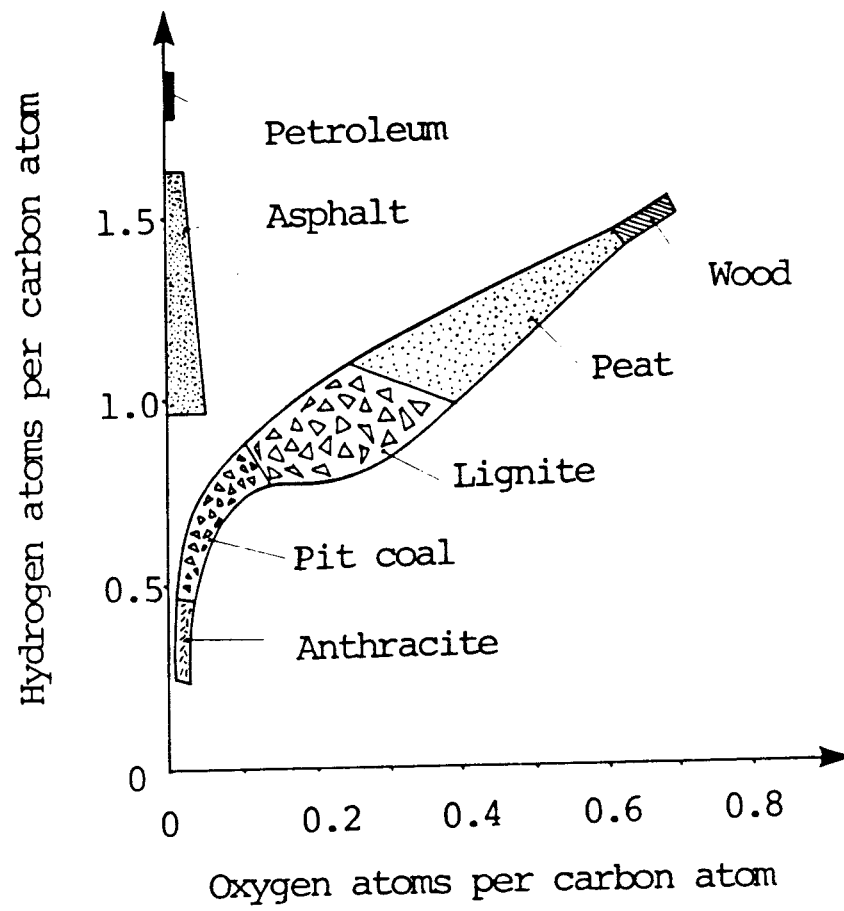


Figure 4. Chemical composition of fuels /20/

Peat is very reactive and can easily be changed by thermochemical conversion, e.g.

- pyrolysis
- gasification
- liquefaction

to cleaner and more convenient fuels. The purpose of this conversion is to transform peat to liquid or gas by reduction. Direct fermentation of peat to methane has been discussed as a possible technique.

There are, however, recent plans to exploit about 10-20 % of the Swedish peatlands for fuel production.

In table 2 four solid fuels are compared.

Table 2. Chemical composition and properties of some solid fuels /20/.

| | | Coal | Lignite | Peat | Wood |
|---------------------------------------|-------------------|-----------|-----------|-----------|-----------|
| Chemical composition: | | | | | |
| Carbon (C) | weight % | 76-87 | 65-75 | 50-60 | 48-55 |
| Hydrogen (H) | weight % | 3.5-5.0 | 4.5-5.5 | 5-7 | 6-7 |
| Oxygen (O) | weight % | 3-11 | 20-30 | 30-40 | 38-43 |
| Nitrogen (N) | weight % | 0.8-1.2 | 1-2 | 0.5-2.5 | < 0.6 |
| Sulfur (S) | weight % | 1-3 | 1-3 | 0.1-0.4 | 0.02-0.06 |
| Fuel properties: | | | | | |
| Volatile matter | weight % | 10-50 | 50-60 | 60-70 | 75-85 |
| Ash | weight % | 4-10 | 6-10 | 2-15 | 0.1-2 |
| Melting point of ash | °C | 1100-1300 | 1100-1300 | 1100-1300 | 1350-1450 |
| Bulk density | kg/m ³ | 728-880 | 650-780 | 300-400 | 320-420 |
| Eff. calorific value of dry substance | MJ/kg *) | 28-33 | 20-24 | 20-23 | 17-20 |

*) 1 MJ/kg = 0.278 kWh_{th}/kg = 238 Kcal/kg = 2092 Btu/lbs

Some points in connection with the combustion of peat should be noted:

- emissions of sulphur dioxide are usually low, as for other types of cultivated biomass, but they can in some cases exceed the current limiting values
- the emission of nitrogen oxides from peat combustion will be of little significance
- emissions of metals are about the same size from the combustion of coal, peat and wood
- as a rule no restrictions are needed as regards organic emissions from large combustion plants
- the residues contain varying amounts of heavy metals.

As a rule it must be recommended that the peats should be analyzed with respect to pollutants, heavy metals, radionuclides etc before they are burned.

2.2.3.2 Peat as soil substitute or soil improvement

The use of peat for gardening or agricultural purposes has increased rapidly during the last years.

One of the reasons is that the sale of vegetable mould or soil in Sweden has been restricted for some time and the demand is increasing. A great

deal of the peat is utilized in vegetable gardens and greenhouses.

The bulk of the material sold is the reed or sedge type, mostly because it is suited for uses in mixtures with soil. Sphagnum peat may also be used but it is essential that it should be reinforced by additions of fertilizers and lime /5/.

Peat or muck is used in mixtures with mineral soil for four main reasons:

- to improve the physical conditions
- to increase the water-holding capacity
- as a source of humus and nutrients and a substitute for animal manure
- to provide a better rooting medium.

It should be borne in mind that peat is often deficient in plant nutrients, and the possibility that the plants will take up soluble pollutants in the soil-peat mixture should not be neglected.

3 INDIRECT IMPACT

Under the heading of "indirect impact" three phenomena are discussed in this paper. They are all initiated by and dependent on anthropogenic activities but their consequences are less desirable.

3.1 Acidification

The acidification problem is too far-reaching to be treated in detail here and it can suitably be studied elsewhere.

Only a few important points will be mentioned here.

- The complexity of most soils reduces the possibility to of predicting their acidification through acid deposition. It is known, however, that physical and mineral properties of soil are parameters involved.
- The amount and composition of organic matter in soil is important as well as the content and the activity of microorganisms.
- For several metals, increased mobility due to higher acidity in soil is accompanied by increased solubility, and free metal ions can be available to plants, at least to vascular plants.
- Very little is known about the availability of metals to microorganisms in acid soils.

- The complex- or chelate-binding compounds become less stable at low pH-values.
- Acidifying fertilizers can be responsible for at least half of the acidifying effect in some soils /35/. Compare the pH changes in the following table.

Table 3. The pH changes in soil treated with different fertilizers and two strong acids /6/.

| <i>Fertilizer</i> | 100 kg N | | 200 kg N | | 500 kg N | | 1 000 kg N | Δ pH per 100 kg N |
|---------------------------------|------------|-------|----------|-------|------------|-------|------------|--------------------------|
| | I | II | III | I | II | III | | |
| <i>Calcium nitrate</i> | +0,05 | -0,04 | +0,04 | +0,23 | \pm 0,00 | +0,10 | +0,02 | |
| <i>Calcium ammonium nitrate</i> | +0,04 | -0,14 | -0,22 | -0,08 | -0,48 | -0,50 | -0,05 | |
| <i>Urea</i> | -0,07 | -0,08 | -0,24 | -0,19 | -0,50 | -0,76 | -0,08 | |
| <i>NPK 20-5-9</i> | \pm 0,00 | -0,10 | -0,20 | -0,24 | -0,59 | -0,96 | -0,10 | |
| <i>Ammonium sulphate</i> | -0,13 | -0,33 | -0,68 | -0,37 | -0,97 | -1,22 | -0,34 | |
| <i>Nitric acid</i> | -0,06 | -0,04 | -0,12 | | | | | |
| <i>Sulphuric acid</i> | -0,01 | -0,09 | -0,36 | | | | | |
| <i>Manure</i> | +0,02 | -0,04 | +0,11 | +0,23 | +0,22 | +0,33 | +0,05 | |

Period I: 6.6.72-16.8.72; Period II: 6.6.72-8.5.73; Period III: 6.6.72-30.8.73.

3.2 Leaching

Human impact influences the leaching rate in several ways for instance through fertilization, irrigation and the choice of crops.

During its passage through the soil the water dissolves salts, induces ion exchanges and hydrolytical processes and enhances chemical weathering. Consequently the composition of the percolating water is successively changed both qualitatively and quantitatively.

When the amounts of rainfall or irrigation water entering the soil become greater than its water-holding capacity, losses by percolation will occur. Leaching of cations added to the soil in fertilizers is affected by the soil's cation exchange capacity (CEC). Humic matter has a very high CEC and peat soils tend to hold the nutrients and prevent their leaching.

As the elements nitrogen and phosphorus mostly accelerate the eutrophication processes in a lake, their leaching is of special interest /25/.

It is hardly possible to generalize the role of chemical fertilizers in nitrate losses through leaching. Among other things the leaching rate of nitrogen varies with the type of crop, the amount and time of fertilizer applied, the soil permeability, the precipitation rate and irrigation, the evaporation hydrology etc.

The leaching rate is also dependent on the choice of fertilizer. Ammonium-containing fertilizers cause a depression of soil pH-value in accordance with the expected acidifying

effect in soil through the microbial nitrification of ammonium.

Nitrogen losses from old, unfertilized wooded ground are usually very low, around 1 to 2 kg hectare⁻¹ year⁻¹ /39/. As the need for easily available nitrogen is the limiting growth factor for Swedish forests follows that the content of ammonium and nitrate is low in run-off water.

Increased concentrations of nitrogen in surface or groundwater can usually be explained by fertilization, clear felling, drainage, liming etc. Forest fertilization with ammonium nitrate has been followed by increased concentrations of nitrate both in streams and in groundwater /19/.

As discussed earlier, it is typical of most peats that they contain a large amount of nitrogen but are poor in phosphorus and potassium. When fertilizing forests on peatland it is important to choose a phosphorus fertilizer with low solubility to minimize the leaching /19/.

Potassium can migrate to the groundwater more easily than phosphorus, but negative effects of this element are not observed.

The supply of nitrogen to peat soils, like the supply to mineral soils, can entail leaching. When dissolved preferably in the soil solution the NO₃ nitrogen moves fast down to drainage or groundwater. Likewise in peat, ammoniated nitrogen has a great mobility. To minimize the leaching rate of nitrogen, the type of peat and the amount of fertilizer applied are of importance /19/.

When 60 kg nitrogen hectare⁻¹ is given, an amount now recommended, the leaching rate is negligible however.

In connection with clear-felling and nitrogen leaching /38/, one factor may be the harvesting technique. The trend is to use more and more of the biomass (removal of the whole tree including branches and stump), a technique which can be expected to have different ecological consequences.

The problems of leaching, both from arable soils and from forest soils, have been considered and discussed in several references, e.g /37, 41, 42/.

The arable land in the south of Sweden is well fertilized and the phosphorus status of the soil is also very high. Lake Ringsjön in Central Skåne is of importance both for supplying drinking water and for recreation and fishing. Today this lake is seriously eutrophicated. In /10, 26, 27/ high nutrient losses were reported. The losses of phosphorus were especially high .

Both surface and drainage waters were analyzed from different points in the catchment area. The nitrogen concentration in the surface water amounted to around 60 % of that in the drainage water. For phosphorus the case was exactly the reverse in this area, and the total phosphorus concentration was three times greater in surface water than in drainage water.

A calculation of the transport of nutrients is given in the following table.

Table 4. Transports of nutrients and eroded material with surface and drainage water to lake Östra Ringsjön (to be compared with transports calculated for arable land and forests of larger areas in Sweden) /10/.

| Ground | Run off (mm) | Transport (kg·hectare ⁻¹ ·year ⁻¹) | | | | |
|---|--------------|---|-------|--------------------|--------|------|
| | | NO ₃ -N | Tot-P | PO ₄ -P | Part-P | Susp |
| Arable land surface water | 60 | 3.4 | 0.16 | 0.09 | 0.06 | 44 |
| Arable land drainage water | 519 | 48 | 0.46 | 0.28 | 0.17 | 46 |
| Forest | 579 | 4.6 | 0.08 | 0.02 | 0.06 | 23 |
| ----- | | | | | | |
| Arable land [*] The South of Sweden | 302 | 39 | 0.37 | 0.19 | - | - |
| Forest ^{**} The whole of Sweden | - | 0.3 | 0.06 | 0.02 | - | - |

* from /9/
** from /4/

It is well known that the extractibility of most metal elements in soil is greatly dependent on the acidity of the system and the residence time of heavy metals in forest soils is given in reference /35/.

3.3 Soil decomposition

In some references the settling of peatsoils is discussed with regard to a lake depression in Sweden. In Kvismar Valley in Närke it is observed that not only the peat soils but also clay soil mixed up with gyttja had settled around 50 centimetres during the first 50 years after drainage. During the following 30 years the soils in this area decreased 0.7 centimetres year⁻¹ on an average /15, 33/.

Three factors may be mentioned to explain the settling of soils:

- the shrinkage of peat soils through the drawing off of groundwater
- the shrinkage of gyttja soils and generation of permanent cracks and fissures
- oxidation of organic matter.

Increased exploitation of peatlands initiated by drainage will rapidly oxidize the organic matter.

When plants become senescent they are invaded by microbial decomposers but the bulk of decomposition does not take place until the dead vegetation comes in contact with the soil. Once on the ground the plants are subject to attack by microbes, bacteria, yeasts, actinomycetes and fungi and the decomposition rate is accelerated.

As the bacteria and fungi work on the plant debris they assimilate the nutrients and incorporate them in living matter. At this point the nutrients are still unavailable for recycling /30/. Both bacteria and fungi are shortlived and the nutrients are released or mineralized and become available for uptake again.

In terrestrial ecosystems bacteria and fungi play the major role in decomposition /8/. Organic compounds vary greatly in their rate of decomposition. In terms of their ease of decomposition they may be listed as follows

- sugars, starches, simple proteins
- crude proteins
- hemicelluloses
- cellulose
- lignin, waxes, fats.

The soil microorganisms must not only have nutrients for their tissue synthesis but energy as well. Organic matter contains considerable potential energy.

The more common simple decomposition products resulting from the activity of soil microorganisms may be listed as follows:

- carbon CO_2 , CO_3^{2-} , HCO_3^- , CH_4 ,
 elemental carbon
- nitrogen NH_4^+ , NO_2^- , NO_3^- ,
 gaseous nitrogen
- sulphur S , H_2S , SO_3^{2-} , SO_4^{2-} , CS_2
- phosphorus H_2PO_4^- , HPO_4^{2-}
- others H_2O , O_2 , H_2 , H^+ , OH^- , K^+ , Ca^{2+} ,
 Mg^{2+} etc.

A lesser amount of carbondioxide reacts in soil and produces i a carbonates and bicarbonates of calcium, potassium and magnesium. These compounds are readily soluble and may be used by higher plants or lost by drainage.

Proteins are split up into aminoacids and by means of enzymic hydrolysis they yield ammonium compounds. A large number of heterotrophic organisms are involved in these reactions.

Under aerobic conditions ammonium is enzymically oxidized to the nitrate form. The organisms in this case are all specialized and autotrophic, i.e. they obtain their energy from the oxidation of mineral constituents. Nitrates are assimilated

by plants and are also subject to leaching losses. Hydrogen ions are obtained through the oxidation of ammonium ions.

In poorly drained and in acid soils nitrates and nitrites may be reduced by chemical as well as biochemical reactions and free nitrogen or oxides of nitrogen may be evolved.

Many organic compounds contain sulphur and in several cases organic subsoils contain both inorganic and organic sulphur (gyttja). In /33/ the consequences of high sulphur content in soil are discussed and the chemical reactions between different compounds are elucidated. By draught and drainage the oxidation of sulphur will dominate. It may be oxidized to SO_4^{2-} and the soils will be acidified.

Both inorganic and organic forms of phosphorus occur in soils and both are important to plants as sources of this element. The kind of phosphate present in soil varies with the pH in the soil solution. In alkaline soil the HPO_4^{2-} is apparently most common and at pH-values around 4-5 H_2PO_4^- tend to prevail.

In general H_2PO_4^- is considered more available to plants than other P-ions. Organic phosphorus compounds are mineralized by microbial activity to H_2PO_4^- and HPO_4^{2-} . Small amounts of phosphorus in complex mineral combinations are usually very slowly available.

4 CONCLUSIONS

The effects of human impact can as well accelerate as counteract the development of a lake or a bay, but most influences increase the ageing rate during the different stages, for instance:

- During the eutrophication: Fertilization of arable land in the catchment area may lead to nutrient losses, above all of phosphorus and nitrogen, with increased eutrophication rate as consequence.
- Clear felling of forests combined with fertilization and drainage may give rapid release of nutrients to surrounding lakes.
- Fertilizers containing ammonium can be enzymically oxidized under aerobic conditions to the nitrate form, leading to a decreasing soil pH with increased solubility and mobility of cations.
- Outlets of polluted waste water from industries and households may accelerate the ageing rate of the recipient.
- Aquaculture may result in a release of phosphorus and other pollutants in inland waters while nitrogen is most important as a pollutant in coastal areas.
- Ditching of surrounding areas may lead to changes in the water balance and the water chemistry in the recipient.
- In association with the terrestrialization: Drainage of a lake to get new arable soils leads to oxidation in the upper soil layers. Organic and inorganic sulphur may be oxidized to SO_4^{2-} and the soil will be acidified. The solubility and mobility of heavy metals and radionuclides can increase.
- More and more aerobic conditions in the upper layers of the soil lead to enzymic oxidation of nitrogen compounds to nitrate and a lower pH as a consequence.

The release and transport of pollutants from sediment and organic soils may be influenced by for instance the following factors:

- Oxidation processes and decomposition in organic soils due to drainage and cultivation.
- Uptake of metal ions via roots in connection with crop production and grazing.
- Lowering of pH in soils due to acid rain may change the solubility and perhaps also the plant availability of metals.
- Use of peats in energy production may possibly lead to dispersion of pollutants in the environment.

To sum up: the effects of human impact which are estimated to be of predominant importance in connection with the eutrophication of a lake or a bay seem to be associated with acidification and leaching processes. After the terrestrialization of a wetland area the consequences of oxidation and biochemical decomposition of soil substances due to cultivation may be important.

The effects mentioned above are examples of impacts that are common or may be expected today. Other human activities in the future may naturally lead to hitherto unknown consequences.

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