Patterns and variability of Phosphate and Heavy Metals in sediments of two Shallow Lakes

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I contribute this work to her and to my two daughters Emmy and Vera.

To Els, Emmy and Vera

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Chapter I

CONCLUSIONS AND SUMMARY

1.1 GENERAL CONCLUSIONS

Lake sediments can act as a chemical reservoir for many compounds. Sometimes they can act as a new source for phosphorus and partly negate the effects of water treatment before discharge. From the sediments of lake Westeinder and lake Elfhoeven, two unstratified shallow lakes in the Netherlands, thirty totally undisturbed cores were taken. The cores were sliced and analysed for twenty elements and compounds

- The three-dimensional distribution of most elements was widely scattered while, with exeptions, correlation between the elements was very low. From the statistical properties observed, a two stage strategy is developed in order to reduce the effort and cost of future sampling programs. The first step gives an impression of the composition of the lake-bottom. On the basis of this, the number of samples in the second step is computed.
- An improved type of corer is developed. It consists of a main frame fitted out with interchangeable accessories, allowing adaptation in the field to the specific types of sediment to be encountered.
- Most elements do not show a vertical pattern in their distribution. Phosphorus, copper and to a lesser extent lead, titanium and zinc do. The steep concentration gradients observed indicate, that turbation in sediments does not significantly effects vertical distribution.
- Based on statistical grounds it is argued that standards for toxic and hazardous materials can only work if stated in stochastic terms.
- Apparently for the first time, a quantitative phosphate budget is made for a fifty cm thick sediment layer. The amount of phosphate due to eutrophication is found in the sediments with an uncertainty of about 20 %. The effects of downward percolation on the transport rate of phosphorus in sediments is clearly demonstrated.
- A quantitative copper budget could not be made, probably due to transport mechanisms different from those for phosphorus. Part of the lake showed a very high concentration in the upper toplayer.

1.2 SUMMARY

It can be stated that the quality of surface water has deteriorated in time. Many impurities can be included in the sediments. Sediments form a chemical reservoir and reduce the concentrations of many chemicals, compounds and materials in the water standing above. Surface water quality can be improved by treating sewage and industrial wastes before discharge onto open water. After this has taken place, the lake sediments can act as a new source of pollution, partly negating the effects of treatment. As a contribution to the study of these effects in the aquatic system, the sediments of two unstratified shallow lakes, lake Westeinder and lake Elfhoeven, both located in the Netherlands, were investigated. Lake Westeinder is part of a balancing system of a water-board, Lake Elfhoeven is part of a polder system. The surface water that feeds the lakes contains only small amounts of suspended solids. 30 totally undisturbed core-samples with a length of 50 cm and a diameter of 11 cm were taken. These cores were sliced. The horizontal and vertical distribution of the following elements were determined; Al, As, Ca, Cr, Co, Cu, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti and Zn. Furthermore, the watercontent, the ortho-phosphate and total-phosphate concentrations of the interstitial water and the total-phosphate content of the sediment. The fractionation of iron-compounds and by implication of phosphates in the sediments were studied through Mossbauer Spectroscopy.

The measured concentrations of most elements show considerable variation, as well over the lake-area as in depth. The observed distributions originate as a consequence of two kinds of mechanisms: concentration and dispersion. Concentration mechanisms increase variability and may lead to structures that can be recognized. Dispersion mechanisms break down variability and erase structures that may have been present.

The distribution of several elements measured in the sediments of lakes Westeinder and Elfhoeven appeared to be so widely scattered that research on patterns of these elements appears to be of no consequence, unless many samples are taken. Only in the case of copper and phosphate concentrations patterns were observed in the solid sediments that justified further evaluation. Future research on the patterns of these elements probably will give much more reliable information on the function and role of sediments in the aquatic system both qualitatively and quantitatively. Definition of the consequences of spatial scatter for the sampling strategy and the analysing program can reduce the effort and costs of research programs considerably.

Disregarding the occurrence of patterns in the spatial distribution of the elements, the statistical properties of the data were considered. The elements are arranged in order of their distribution over the lakearea and to their distribution in depth of the sediments. In the sediments of lake Westeinder; standard deviations vary between 22 % for chromium and 112 % for ortho-phosphate as percentage of the samplemean. In the sediments of lake Elfhoeven these vary between 7 % for chromium and 114 % for lead. The standard deviation of arsenic is 100 % of the mean in both lakebeds.

It thus appeared that for some elements the concentration mechanisms are of prime importance (ortho-phosphate, lead and arsenic), while for most other elements possible effects are invisible (chromium, nickel). Concentration mechanisms operate on a spatial scale and on a time scale. The distribution in depth for instance reflects the variation of the inputs and thus reflects the time scales of different processes. Only in the case that this depth-dependency is on the same scale or on a larger scale than the thickness of the slice, this pattern can be observed.

The spatial variation of arsenic in vertical direction was measured on a centimeter scale, while in horizontal direction a scale of several hundred to a thousand meters was applied. As a spatial structure of arsenic is not visible within this scale of sampling, the processes that cause the arsenic content can be concentration mechanisms, that operate only locally on smaller scales than the scale of sampling. The result is an accumulation on the scale of one particular slicing. In lake Elfhoeven two cores were taken two meters apart and even here, a completely different picture was observed. The process thus concentrates on a scale larger than ten cm being the diameter of the core, but not on scales as large as several hundred meters. We can not identify the mechanisms, responsible for this effect. The measurements show such a wide variety, that we can not even start to make an assumption on the cause.

For the elements arsenic and lead and for ortho-phosphate the last number of years a reduction in the surface water could be observed. The drastic arsenic decrease in surface waters was not quantitatively reflected in the vertical profiles of the sediments. The large variation of arsenic was observed in both lakes in depth as well as over the area as a whole.

For copper and phosphorus spatial structures were observed, meaning that at least one process operates at a spatial scale, equal to our sampling scale. This is important for future research, since the spatial sampling scale on which these processes can be investigated is now known, even though roughly, as well as the statistical properties.

In both lakes, phosphorus shows a vertical structure but, in the case of lake Westeinder, also a horizontal one. The pattern, decreasing in depth, reflects the increased phosphate loading since the sixties. In eutrophication research, phosphate balancing studies of surface waters often are a starting point. Phosphate balances are based on water balances and phosphate concentrations. Retention by sediments or release from sediments is usually used as balancing post. In this study a more direct approach is used. A phosphate budget of the sediment itself is reported, using the phosphate concentrations of the sediments and interstitial water as input data for direct computations of the phosphate input from lakewater to the sediment system. The balance was found

to be quantitatively correct and is presented in chapter VII. The extra P-load is quantitatively found, accumulated in the toplayers of the sediment. The observed high total phosphate concentration decreases in depth and stabilizes between 10 to 30 cm depth below the interface to a constant value, part of it corresponding to a dynamic equilibrium before the onset of man-made eutrophication. The horizontal structure roughly corresponds with that, as found for copper and a positive correlation was observed between the phosphorus accumulation in the toplayers of the sediments and the infiltration ratio. For sediment the phosphate the main transport medium is found to be the downward percolating water.

Since increased eutrophication is known to have started during 1969 and the amount of phosphate is quantitatively accounted for, we are now in a position to approximate the vertical transport rates in the sediments (chapter VII). This can be important for future developments of a model. As noted before, a difference between the two lakes can be observed. The transport rate appears to be inter-dependent on the infiltration rate of the water giving rise to higher penetrations in depth of phosphates in the lake Westeinder sediments. This is consistent with the observed depth distribution for copper.

The distribution of copper in lake Westeinder shows a strong vertical structure and a strong horizontal pattern as well, both phenomena can be observed in the one cm thick toplayer. In one part of the lake large amounts of copper were found, accumulated in the fist top cm of the sediments. These large amounts can not be explained by copper inputs from the lake-water only. The horizontal structure can partly be explained by e.g. the spatial differences in infiltration ratio and the rapid binding of copper by the sediments. The copper balance however, is not quantitatively correct. The amount of copper, present in the utmost toplayer of the sediments exceeds the maximum yearly input by a factor 10. Transport of the sediments from the bounding Ringvaart canal to the lake and locally high infiltration ratios in the south-western part of the lake are discussed as some of the possible causes.

Based the observed vertical distribution of copper- and total-phosphate contents of the sediment and of the ortho- and total-phosphate concentration profiles of the porewater, it can be concluded, that dispersive effects of bioturbation and windturbation in both lake Westeinder and lake Elfhoeven are of less importance than often assumed.

Some practical consequences of this work are discussed in chapters VIII and IX. The observed spatial scatter is considerable and differs strongly per element. The statistical properties of the data are used to develop a sampling strategy. To maximize efficiency, a sampling program can best be executed in two steps. The first step gives an impression of the composition of the lakebottom and indicates what cost and effort will be required in a second step in order to provide the information which is lacking and diminish all uncertainties.

The sample-size for each element during the first step depend on the variations in both lake-bottoms from which little was known at the time of sampling. A first test of 5 to 6 cores spread over the total area can be regarded as reasonable and sufficient to establish the elements in the sediments of both lakes. Renewed sampling showed the reliability of these propositions, applied to the same lakes. It has shown the same reliabilityin other lakes as well.

The measured concentrations of elements are compared to the legislation for toxic and hazardous materials in the Netherlands. Based on statistical grounds, it is argued that standards for these types of elements and compounds can only be operative if stated in stochastic terms.

To trace existing structures in the water laden toplayers of the sediments, it is essential that the cores are undisturbed. Even the equipment which was applied during this study did not provide totally undisturbed sediment cores under all circumstances. We had to discard several semi-disturbed and unreliable cores before we had obtained the 30 to our satisfaction undisturbed cores, that form the basis for this study. To solve this problem we had to develop sampling equipment with which totally undisturbed cores from almost any type of sediments from river-bootoms and lakes can be obtained. The equipment consists of a main frame, fitted out with inter-changeable accessories, allowing adaptation in the field to the specific types of sediment to be encountered. For the closing mechanism at the lower end three designs were developed: an open head for clayey-type sediments and cutter heads that can be closed mechanically or pneumatically for softer types of sediments. This equipment is now commercially available.

1.3 SAMENVATTING

STRUCTUUR EN SPREIDING VAN CONCENTRATIES FOSFAAT EN ZWARE METALEN IN BODEMSEDIMENTEN VAN TWEE ONDIEPE MEREN

Tesamen met het verslechteren van de waterkwalitiet zijn vele verontreinigingen in de onderwaterbodem geaccumuleerd. Sedimenten gedragen zich als een opslagreservoir en verlagen de concentratie van vele stoffen in het bovenstaande water. De kwaliteit van oppervlaktewater kan worden verbeterd door de behandeling van huishoudelijk en industrieel afvalwater, voorafgaang aan lozing. Na sanering van lozingen kan het sediment echter als interne afgiftebron gaan optreden en de effecten van behandeling deels teniet doen.

Als bijdrage aan de bestudering van deze effecten in het aquatisch systeem zijn de sedimenten van twee niet gestratificeerde ondiepe meren bestudeerd. Hiertoe zijn 30 ongeroerde boorkernen (cores) gestoken met een lengte van 50 cm en een diameter van 11 cm. Deze cores zijn in plakken verdeeld en in elke core is op vijf dieptes het gehalte bepaald van de elementen Al, As, Ca, Cr, Co, Cu, Fe, K, Mg, Mn, Ni, Pb, Si, Sr, Ti, Zn, alsmede het totaal-fosfaat gehalte en het watergehalte van het sediment en de concentraties orthofosfaat en totaal-fosfaat in het interstitieel water. De fractionering van fosfaten, waaronder ijzer-fosfaten, is bestudeerd met Mossbauer Spectroscopie.

De meeste van de gemeten concentraties in de sedimenten vertonen een aanzienlijke spreiding zowel over het oppervlak van de bodem als met de diepte in de bodem. De waargenomen verdelingen vinden hun oorsprong in twee soorten mechanismen: concentratie en dispersie. Concentratie mechanismen doen de spreiding toenemen en leiden tot wellicht herkenbare structuren. Dispersie mechanismen verkleinen de variabiliteit en vernietigen mogelijk aanwezige structuren.

De spreiding in de gehalten van diverse elementen in zowel de Westeinder Plassen als Plas Elfhoeven (Reeuwijkse Plassen) bleek zo groot, dat het speuren naar patronen zinloos is, tenzij veel monsters genomen worden. Alleen voor koper en fosfaat konden patronen worden onderscheiden die een verdere evaluatie rechtvaardigden. Gericht verder onderzoek naar de vragen die hieruit naar voren gekomen zijn zal waarschijnlijk veel en betrouwbare informatie opleveren over de functie en rol van sedimenten in het aquatisch systeem, zowel kwalitatief als kwantitatief. Het vaststellen van gevolgen van ruimtelijke ruis voor de strategie van bemonstering en het daarop volgende analyse programma kan de inspanningen en kosten van research programma's aanzienlijk reduceren.

Na terzijdestelling van mogelijke patronen in de ruimtelijke verdeling van de elementen zijn de statistische eigenschappen van de normaal verdeelde gegevens beschouwd. De elementen zijn gerangschikt volgens hun spreiding over de oppervlakte van het meer (horizontaal) en volgens hun spreiding in de diepte vanaf het sediment-water grensvlak (vertikaal). In de sedimenten van de Westeinder Plassen varieerden de standaard afwijkingen, uitgedrukt als percentage van het gemiddelde, tussen 22% (Cr) en 112% (ortho-P), in de sedimenten van Plas Elfhoeven tussen 7% (Cr) en 114% (Pb). De standaard afwijkingen van de gemeten arseen concentraties in de bodem van beide meren bedroegen 100% van het gemiddelde. Hieruit bleek dat voor sommige elementen de concentratie mechanismen het belangrijkste zijn (o-PO4, Pb, As) terwijl voor andere elementen mogelijke effecten niet zichtbaar waren (Cr, Ni). Concentratie mechanismen hebben een ruimtelijke schaal en een tijdschaal. Verwacht kan worden dat deze schalen verschillend zijn. De diepteverdeling bijvoorbeeld geeft een beeld van de input-variatie en daarmee van de tijd. Alleen wanneer deze diepte afhankelijkheid op dezelfde of op grotere ruimtelijke schaal dan de plakdikte werkzaam is, kan het patroon waargenomen worden.

Bij arseen is de variatie in de diepte gemeten op een schaal van centimeters, in horizontale richting op een schaal van enkele honderden meters tot een kilometer. De ruimtelijke structuur is binnen deze schaal van bemonstering niet zichtbaar. De processen die het arseen gehalte bepalen kunnen nu concentratie mechanismen zijn, die lokaal effect sorteren op een schaal, kleiner dan die van bemonstering. Dit resulteert in een accumulatie in een plak van de core.

In plas Elfhoeven zijn twee cores genomen op een afstand van twee meter. Zelfs hier werd een volledig verschillend beeld waargenomen. Er trad dus een concentratieproces op, op een horizontale schaal die groter is dan 10 cm, de monsterdiameter, maar kleiner dan enkele honderden meters. het voor dit effect verantwoordelijke mechanisme is niet geidentificeerd. De arseenreductie in het oppervlaktewater van de laatste 10 jaar is niet kwantitatief terug te vinden in de vertikale profielen in het sediment. Dit geldt ook voor lood en orthofosfaat in het poriewater. de grote spreiding is in beide meren zowel met de diepte als over het sediment oppervlak gemeten.

Ruimtelijke structuren zijn waargenomen in de concentraties van koper en fosfaat. Hieruit blijkt dat tenminste een proces werkzaam is op een ruimtelijke schaal, gelijk aan de schaal van bemonstering. Dit is belangrijk voor verder onderzoek, aangezien de ruimtelijke schaal waarop bemonstering ter bestudering van deze processen moet plaatsvinden nu ruwweg bekend is, evenals de statistische eigenschappen van de monstername.

Het fosfaat gehalte in het sediment vertoont in beide meren structuur over de vertikaal en in de Westeinder Plassen ook in horizontale richting. Het waargenomen dieptepatroon weerspiegelt de sinds de zestiger jaren toegenomen fosfaatbelasting.

In het eutrofieringsonderzoek vormen fosfaatbalansen vaak een vertrekpunt. Ze zijn gebaseerd op waterbalansen en fosfaat concentraties van het water. Het is gebruikelijk dat de balans sluitend wordt gemaakt door de aanname dat de verschillen toe te wijzen zijn aan retentie door het sediment of afgifte vanuit het sediment. In deze studie wordt een andere aanpak gebruikt. Met gebruikmaking van de gemeten fosfaat concentraties in sediment en poriewater op verschillende dieptes in de bodem is een fosfaatbalans van het sediment opgesteld waaruit de input vanuit het water naar het sediment systeem direct berekend is (hst. VII). Deze fosfaatbalans van het sediment bleek kwantitatief te kloppen: de extra fosfaatbelasting werd in het sediment teruggevonden, geaccumuleerd in de toplagen. De hoge totaal-fosfaat gehalten in de toplagen van het sediment nemen met de diepte af en stabiliseren zich op dieptes tussen 10 en 30 cm. Deze constante gehalten bestaan voor een deel uit in dynamisch evenwicht verkerend fosfaat, wat reeds aanwezig was voor de sterke toename in de eutrofiering. De gevonden horizontale structuur correspondeert in grote lijnen met de in de kopergehalten gevonden structuur, die onderstaand beschreven wordt. Ook zijn de fosfaat accumulaties in de toplagen positief gecorreleerd met de infiltratiesnelheid. Het infiltrerende oppervlaktewater is een belangrijk transportmedium voor fosfaat in het sediment. Aangezien de toegenomen eutrofiering rond 1960 begonnen is en ook de hoeveelheid fosfaat die daarmee gemoeid is ruwweg bekend is, is nu een eerste benadering van de vertikale transportsnelheden in het sediment gemaakt. Dit is mogelijk van belang voor het verder ontwikkelen van modellen. Er bestaat een verschil tussen de twee meren. De transportsnelheid blijkt afhankelijk te zijn van de infiltratiesnelheid van het water, hetgeen resulteert in een dieper doordringen van grotere hoeveelheden fosfaat in de sedimenten van de Westeinder Plassen. Dit komt goed overeen met de waargenomen diepteverdeling van koper.

De verdeling van koper laat een duidelijk vertikaal en een duidelijk horizontaal patroon zien, beide waargenomen in een 1 cm dikke toplaag van de onderwaterbodem van de Westeinder. In het zuid-westelijk deel van dit meer zijn grote hoeveelheden koper in de bovenste cm geaccumuleerd. Deze grote hoeveelheid kan niet verklaard worden uit de koperinput vanuit het water. De koperbalans is kwantitatief niet correct: de hoeveelheid koper in de bovenste 1 cm dikke laag is ca. 10 maal zo groot als de maximale jaarlijkse input vanuit het water. Als mogelijke oorzaken hiervoor worden o.a. besproken het transport van gesedimenteerd materiaal vanuit de langs- en deels instromende Ringvaart en een lokaal hogere infiltratiesnelheid in het zuid-westelijk deel van het meer.
Op basis van de gemeten vertikale profielen van koper en totaal-fosfaat in het sediment en van ortho- en totaal-fosfaat in het poriewater blijkt dat in beide meren de dispersieve effecten van bioturbatie en windturbatie veel minder belangrijk zijn dan vaak wordt aangenomen.

In de hoofdstukken *VIII* en *IX* worden enkele praktische consequenties van dit onderzoek behandeld. De waargenomen ruimtelijke ruis is aanzienlijk en verschilt sterk per element. Met de statistische eigenschappen van de gegevens wordt een bemonsterings strategie ontwikkeld. Een monsterprogramma is *het meest effectief wanneer het in twee stappen wordt uitgevoerd.* De eerste stap geeft een indruk van de samenstelling van de onderwaterbodem en duidt de noodzakelijk vereiste inspanning en kosten aan om in een tweede bemonsteringsstap de ontbrekende informatie te verkrijgen en onzekerheden te ver*minderen. de steekproefgrootte in de eerste stap is steeds* afhankelijk van de spreiding in de onderwaterbodem. Deze was ten tijde van het onderzoek onbekend. Het bleek in beide meren dat een eerste steekproef van 5-6 cores redelijk is voor veel elementen. Hernieuwde monstername toonde de *juistheid van deze voorspelling aan in dezelfde meren alsook* in andere.

De gemeten concentraties zijn vergeleken met de wettelijke regelingen in Nederland op het gebied van schadelijke en toxische stoffen. Op statistische gronden worden normen voor dit type elementen en verbindingen geacht alleen dan operationeel te kunnen zijn als ze een statistisch element bevatten. Om bestaande structuren in de vaak dunne, waterrijke bovenste sediment lagen te kunnen opsporen moeten de cores ongeroerd zijn. De apparatuur die in deze studie gebruikt is leverde niet in alle omstandigheden ongestoorde sediment cores. Diverse geroerde dan wel onbetrouwbare cores moesten worden weggegooid, alvorens de 30 ongeroerde cores zijn verkregen die gebruikt zijn voor dit werk. Om dit probleem op te lossen is bemonsterings apparatuur ontwikkeld, waarmee ongeroerde cores uit vrijwel elk type bodemsediment verkregen kunnen worden. Het modulair opgebouwde apparaat bestaat uit een basiseenheid die uitgewisseld kan worden met uitwisselbare onderdelen. Zo wordt een aanpassing in het veld mogelijk, afhankelijk van het type sediment dat wordt aangetroffen. Voor de onderzijde van de core zijn drie uitwisselbare snijkoppen ontwikkeld, een open snijkop en twee snijkoppen die in het *sediment mechanisch of* pneumatisch kunnen worden afgesloten.

Chapter II

INTRODUCTION

2.1 DEFINITION OF THE PROBLEM

During the past 20 years waterquality aspects have become more and more important. Care became obligatory after a national law against water pollution came into effect in 1970. On the basis of this law, the waterboards were and are entitled to prohibit discharges of wastewater without license. This gave the water-boards in principle the opportunity to ban dangerous or undesirable matters from receiving waters. Many wastewater treatment plants have been built since that time. Their main function is to reduce the organic load of the surface water. As the removal of organic material from wastewater is not complete, a loading of the surface waters still exists. Chemicals in those inputs are organics, but also phosphates, metals, among which heavy metals and other possible toxic elements like arsenic. The Waterboard of Rijnland is responsible for the lakes that were investigated in this study. A routine sampling program is carried out in the surface waters in the administration area. The results are published in annual reports of the waterboard (Rijnland, 1980, 1981, 1982 and 1983).

The sources of inputs in surface waters are mainly human activities like industrialization, agriculture and municipal wastewater discharges. They are located both in the Netherlands and abroad. Inputs are mainly transported by the rivers Rhine and Meuse. The surfacewaters in the Netherlands were and still are loaded with large amounts of compounds, as a consequence. The chemicals are either dissolved or adsorbed on suspended solids. Many substances, that enter the lakes are degradable or settlable and therefore have been settled, before the water flows out of the lake. The sediments accumulated contain large amounts of chemical compounds from the water, thus acting as a sink for these elements and compounds in natural systems.

Between the sediments and the surfacewater a constant exchange of material occurs. The sediment-water interface separates the solid sediment, containing the interstitial water, from the overlying waterbody. Sorption processes and solubility within the sediments and transport processes across the sediment water interface are important in control of the dynamic chemical processes between the sediments and the overlying water. Many studies have been put together in reviews published in J.W.P.C.F. Some of these are by Ku et al (1973, 1974), Powers (1977), Sanville (1978) and De Pinto (1981). Both position and composition of this interface change as a consequence of sedimentation of particles from the water body. Arrival of sediment particles and entrapment of water in the pore space between the particles are considered to be two major fluxes of materials across the sediment-water interface (Lerman, 1979).

The transport of chemicals across the interface is caused by transport and dispersion mechanisms like mixing of the sediment and the direct overlying waterlayer. The advective transport processes can be subdivided in sedimentation, upward and downward flow of water due to the differences in levels of ground- and surfacewater and the flux of dissolved material into the sediment body following sedimentation, as described above. The exchange processes across the interface are influenced by numerous factors. Some of them are determined by the surface water, but also the sediment characteristics play an important role (Sly, 1981). The sediment can be characterized in different ways: chemically, physically and biologically. The characteristics of the bottom material, for instance the geochemical properties but also temperature profiles (Lappalainen, 1982), determine the adsorption capacity for elements present in the overlying surface water. This will help to determine correctly the fate of adsorbed compounds, but also to predict important parameters of the processes of release like conditions under which release occurs and the duration and intensity of release processes.

People like clear water in their immediate surroundings, either to swim in, to fish or to paddle. Lerman (1979) called this the 'limnetic drive' of man. The governmental policy reflects this popular desire by legislation and aimes at a reduction of the inputs in surface waters with improvement of water quality for man and environment as main goal. In the Netherlands these objectives are embodied in an action program for water (Water Action Programme: 85-89). Some classical examples on improvement of water quality outside the Netherlands are lake Washington (Shapiro et al, 1971), the Swiss lakes (Thomas, 1967a, 1967b) and The Wahnbach Reservoir (Bernhardt and Clasen, 1982).
In lake Washington improvement occurred only years after all sewage effluent had been diverted. For the sake of water quality in the deep Swiss lakes, the use of phosphates in washing agents has been forbidden since 1966 in Kanton Zurich in Switserland and phosphate removal was applied, recommended by the Swiss government and obligatory since 1976. This is not yet the case in the Netherlands (Fosfatennota, 1979, Golterman, 1976).

Many measures that reduce inputs often do not rapidly result in improvement of the water quality, because the sediment, acting as a chemical reservoir, is able to release different adsorbed materials again, when the concentration in the water is lowered (a.o. Ahlgren, 1977 and 1978, Bates and Neafus, 1980). Nevertheless, input reductions are essential to reduce the eutrophication problems. Unfortunately, the reduction of inputs is in most cases not yet accomplished. Tertiary treatment of wastewater is only done on a small scale. In the near future sediment will thus remain to act as a reservoir, rather than being a source. Release processes across the sediment-water interface with other causes like reduction of inputs will consequently determine the effects in the near future. For instance, a lack of oxygen in the environment of the sediment-water interface causes decreasing pH and lowering redoxpotential in the toplayer of the sediments which may induce high release rates of certain elements or compounds from the sediments to the overlying water (a.o. Armstrong, 1979, Balzer, 1980, Frevert, 1979a, Bostrom, 1982, Fillos and Molof, 1976, Fillos and Swanson, 1975). Acid rain depositions do not influence these rates greatly in the carbonate rich lakes (in Rijnland) in the Netherlands, in contrast to other situations as soft water lakes and marshes like for instance exist in Sweden, USA and Canada. In the Netherlands, storage of dredged sediments brings up special problems (van Driel and Salomons, 1982)

In the western part of the Netherlands the shallow waterbodies in lakes are generally well mixed (Huisman and Martijn, 1968). Anoxic periods due to stratification are therefore not likely to occur, although measurements are lacking. Accumulations of chemicals, adsorbed in the toplayer of the sediments can be released into the water easily, due to bioturbation and storm events, resulting in an intensive contact of bottom sediments and surface waters.

Too little information is available now to predict the effect of managing measurements with a desired level of accuracy. Understanding of chemical processes and knowledge of chemicals involved is insufficient. This knowledge is needed to develop quantitative reaction models (Bortleson and Lee, 1974 and Jones and Bowser, 1978). A lack of information exists on the composition of the sediments, on the distribution of chemicals in the sediments and the possible causes for that particular distribution.
Both the horizontal as the vertical distribution in the sediment are important in this respect, as they provide information about the potential release due to processes like bioturbation, windturbation and low oxygen content. Avnimelech (1983) gives an example on this. The vertical distribution gives information about transport processes in the sediments itself under influence of water transport and diffusion. The sediment can act as a memory of the historic development of the loading of a lake (Stumm and Baccini, 1978). The diffusion process plays an important role in the release of elements from the sediments as a.o. stated by Morse (1974).

Knowledge of the distribution of chemical compounds in the sediments also increases the insight in when and where to take samples, that reliably represent the lakebottom. This problem is also discussed by Bricker (1978) and Nielsen et al (1973). The sampling procedure and the number of samples taken are important in this respect. Green (1979) points out that "the assumption of independence of errors is the only one in most statistical methods for which violation is both serious and impossible to cure after the data have been collected. Truly random allocation of samples is the necessary and sufficient safeguard against this violation". This emphasizes the importance of the sampling program very strongly.

To achieve a good picture of the three-dimensional distribution of chemicals in sediments, a still unknown but probably large number of core-samples would be required in the deltaic geochemically heterogeneous western part of the Netherlands, where erosion products from other parts of Europe were and still are deposited (van Eck, 1982). The expectation that the heterogeneity of sediments in this arae will cause additional problems is confirmed in this work. Good knowledge of the spatial structures in the sediments is essential in this respect. Only then, reliable estimates can be made of the sample size.

Results of physical-chemical work, not seldom based on one or very few cores, are often used as input for lake quality modelling. Knowledge of the statistical scatter, however, is essential for correct interpretation of the data. Gathering information on the statistical properties of elements in the field is of great importance, before starting experiments in the laboratory like release experiments and column tests. Definition of the consequences of the observed three-dimensional sctter for sampling strategy and analysing program can reduce the effort and cost of research programs considerably. With the results of this work we are now able to quantitatively predict the required size of a sample in order to reliably describe the composition of the sediments. This prediction is provided with a standard deviation and a level of significance.

In the water budget of Rijnland 65% of the total input of about 1200 million m3/yr originates from precipitation, about 25% is surface water admitted, largely from the rivers Rhine and Meuse. 10% has various sources (Schmidt van Dorp, 1978). This surface water contains considerable amounts of organic material, metals and plant nutrients for quite a long time already (Scholte Ubing, 1980 and yearreports of the International consortium of water supply undertakings in the Rhine catchment area, 1981, 1982). The hydrological situation brings about that Rhinewater also flows through the shallow lakes in this area. The consequences of phosphate inputs in the lakes are important with a timescale of less than a year. The eutrophication and the resulting algal blooms are well known. Therefore, some more attention will be given to phosphorus.
A few balance studies made for lakes in the western part of the Netherlands show a net phosphorus retention by the bottom sediments over the year (Schmidt van Dorp, 1978, Uunk, 1979, de Groot et al, 1979, Pater, 1981 and de Groot, 1981). These balance studies moreover show release of phosphorus from the sediments in summer periods together with retention in the other periods in the lakes Westeinder and Wolderwijd/Nuldernauw (de Groot, 1979 and Uunk, 1979). This is shown in figure 1.
In lake Elfhoeven (Reeuwijk lake area) release in summer periods hardly occurs. Phosphate budget studies for the years 1978, 1979 and 1980, carried out on the basis of an extensive waterbalance, show that release of phosphates of some importance only occurred in spring 1979 and 1980 and in december 1979 (fig 1).

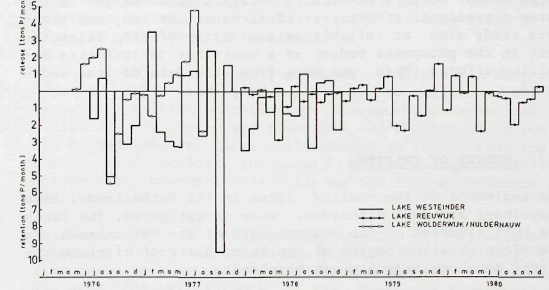


Figure 1: Phosphate budgets of lakes Westeinder, Elfhoeven and Wolderwijd

Waterquality modelling in lakes aims at prediction of changes of the waterquality due to a change in input of one or more elements or compounds (Osborne, 1980, Bogardi, 1980). Several eutrophication models have been developed, that aim to describe the changes in phosphate concentration in lakewater and aquatic systems (Imboden, 1974, Chapra and Sonzogni, 1979, Chapra, 1980 and Bourg, 1982). Most of these models are input-output balance equations in the form of phosphorus mass balances. Transport from or to the sediments is often used as balancing term in the budget, though the processes and transport rates are largely unknown.

The chemical form of phosphorus in water or sediment is difficult to determine. Many tests on the binding of phosphate in sediments have been done. Some examples are Nriagu and Dell (1974) and Nur and Bates (1979), who used a fractionation method to determine the different binding forms as did several others like Williams et al, 1967, 1971a, 1971b, 1976 and 1980, Boust and Saas, 1981, Mayer et al, 1981, Hieltjes and Lijklema, 1980, Furumai and Ohgaki (1982) and Hosomi et al (1981). With Mossbauer Spectroscopy, we tested the chemical fractionation in sediment after Chang and Jackson (1957). We measured the same Mossbauer spectrum before and after the extraction step, in which iron compounds are assumed to dissolve, clearly indicating that this was not the case (Siebers et al, 1982). On the basis of this result we decided to stop working along this line.

In some of the models, the sediment is introduced either as a sink or as a source for phosphorus. This is expressed as a retention or release term in the differential equation, mostly as a balancing post in the phosphorus budget (Kelder-

man, 1980, Kamp-Nielsen, 1975b). It is very difficult indeed to include internal sediment processes in lake modelling because the processes are very complex as already indicated above. Next to efforts to obtain a good insight in the three-dimensional structures of elements in the sediments this study aims at reliable determination of the balancing post in the phosphate budget as a contribution to future modelling efforts. This was done from the data of the sediments.

2.2 SURVEY OF CHAPTERS

The sediments of two shallow lakes in the Netherlands, lake Westeinder and lake Elfhoeven, were investigated. The lakes are both situated in the western part of the Netherlands, in the administration region of the Water Board of Rijnland (in dutch: Hoogheemraadschap van Rijnland).

In chapter III, a description of the lakes is given and the morphometry and hydrology are shortly dealt with. Some factors that influence the sampling strategy like the number of samples to be taken, the sampling locations in the lake, the length, diameter and the quality of the samples are discussed.

In chapter IV, Materials and Methods, all procedures and analysing techniques are given. A short description of the sampling procedure, using a corer, is followed by a description of our handlings with the sediment cores like transport, freezing and slicing. Next *the analytical methods are* discussed. The elements that were analysed are: aluminum, arsenic, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, phosphorus, potassium, selenium, silicon, strontium, titanium, zinc. The orthophosphate and total-phosphate concentrations of the interstitial water were also analysed. The watercontent of the sediment was calculated after drying.

In chapter X, the composition of the lake sediments is discussed *and compared to results of some other research.* The elements were dealt with alphabetically. We tried to locate structures and patterns in the data. Inspection of the data showed, that most of the data show little structure within the lake, neither with depth nor in horizontal direction. Therefore, the assumption is made, that the data show no structure at all. Little information will be lost then and it allows us to treat the data as truly random. For the elements where a structure was observed, phosphorus and copper, this structure and its consequenses are discussed in separate chapters. It is clear, that for most of the elements the discussion on their concentrations is rather descriptive. This is inevitable, however, when the data collected show a more or less stochastic picture.

The spatial variability of the elements is expressed quantitatively as a factor of horizontal or vertical inhomogeneity (with HI and VI as symbols) and is discussed in chapter V.

The data that were collected at certain depths in the sediment were transformed in order to compare their variability in depth as well as over the lake-area. Therefore the terms vertical inhomogeneity (VI) and horizontal inhomogeneity (HI) were introduced. A classification is made next, on the basis of these distribution factors.

The observed structure in the copper profiles has been elaborated. Rapid binding of copper by the sediments, differences in infiltration ratio and transport of sedimented material via the bottom are discussed in chapter VI as possible causes for the large differences in concentrations in horizontal direction. The copper budget is quantitatively not correct, however. Possibilities for further research are mentioned.

In chapter VII the observed distribution and structures of phosphate in the sediments are discussed. The results of a discussion on the water- and phosphate budgets of both lakes are used for calculations on the phosphate budget of the solid sediment. The importance of reliable water budgets *clearly appeared. Statistical* methods are used in chapter VIII to predict optimal samplesizes and expected samplemeans in relation to the observed distribution of the elements in the lake sediments of both lake Westeinder and lake Elfhoeven. As the data are fairly well normally distributed when they are looked upon statistically, it is allowed to use the characterizations of the normal distribution being the average, the standard deviation and the samplesize for these predictions. On statistical grounds, it is considered that norms, as given in the legislation, can only be operative if *stated in stochastic terms.*

The samples were taken with a corer, that was kindly lent to us by prof. H. Ambuehl of the EAWAG Institute in Switzerland. From the experiences with the apparatus (Ambuehl, 1969), it appeared that in some cases no or no reliable sample could be obtained. Therefore we developed and built sampling equipment with which undisturbed cores from sediments, underlying rivers and lakes can be obtained under all circumstances. The design process, the construction and some results are discussed in chapter IX. The project *was financially* supported by the Ministry of Economic Affairs of the Dutch Government. The equipment is constructed from a main frame, fitted with exchangeable accessories, allowing the composition of several sets of equipment, suitable for the expected different field situations.

Chapter III

EXPERIMENTAL AREA AND SAMPLING STRATEGY

3.1 INTRODUCTION TO THE EXPERIMENTAL AREA

The safeguarding of the Netherlands against water and in later years the care for the quality of surface waters are entrusted to waterboards. Some of these organizations already exist since the early Middle-Ages, the maintenance of embankments, including the dunes, as one of the oldest resposibilities. The waterboard of Rijnland exists since about 1200 and is one of the most important of the water-boards in the Netherlands (fig. 2).
The 1200 square kilometers administration area of this board -about 3 % of the total surface area of the Netherlands- is inhabited by 1.2 millions of people -about 8 % of the dutch population- and exists, like other parts of the Netherlands, thanks to dykes, dunes and pumping stations. Without these dykes, more than half of Netherlands 37,000 square kilometers would be sea, including the entire region of Rijnland. (fig. 3). The surface water in the western part of the Netherlands either belongs to a so-called balancing system slightly below mean sea level or a much lower situated polder-water system. The balancing system (called boezem in dutch, fig 3) consists of a number of canals for collection and transport of surface water. Under low tide the system allows gravitational drainage to the sea. In dry periods it acts as a storage reservoir. Interconnected waterways are also used for commercial shipping. Polders are low-lying land areas so that free drainage to the sea is not possible. Most polders are surrounded by dykes. Watermanagement of the polders is controlled with drainage pumping stations and the balancing system: in wet periods water is pumped from the polder to this system, in dry periods water is let in from the balancing system. This allows the possibility that the waterlevel in polders only fluctuates by a maximum of a few centimeters, close to the optimum as required by agriculture.

3.2 DESCRIPTION OF THE EXPERIMENTAL AREA

3.2.1 Selection of the Lakes

Two lakes in the administration region of the waterboard of Rijnland have beenselected to investigate the sediments on the lake-bottom. Both lakes are shallow, but differ in dimensions considerably. Lake Westeinder is part of the balancing system of the water in Rijnland, while lake Elfhoeven is a polder-lake. The waterlevel in the system is

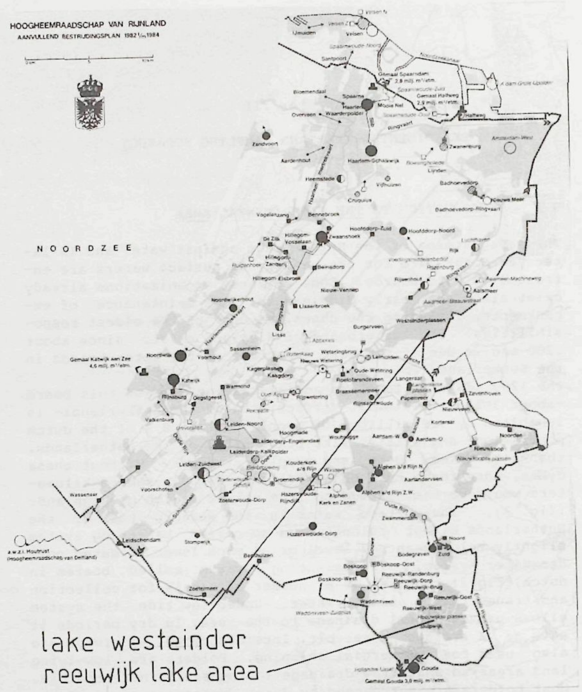


Figure 2: Area of the Waterboard of Rijnland, The Netherlands

higher than in polders as can be seen in fig 3. In lake Westeinder the water percolates downward to the groundwater, the average infiltration ratio is given by Wit (1974) as 1 mm/day and a resistance of the semi-pervious layer of about 2000 days. For reasons of the low water level the infiltration in lake Elfhoeven is small. From Wit an infiltration ratio of between 0 and 0.25 mm/day in lake Elfhoeven can be suggested together with a higher resistance of the semi-pervious layer of about 3000-3500 days. The lakes were chosen on the basis of earlier investigations, the availability of data and knowledge of the field situation. Lake Westeinder is the largest lake in the management area of Rijnland. Lake Elfhoeven is about ten times smaller and is considered to be

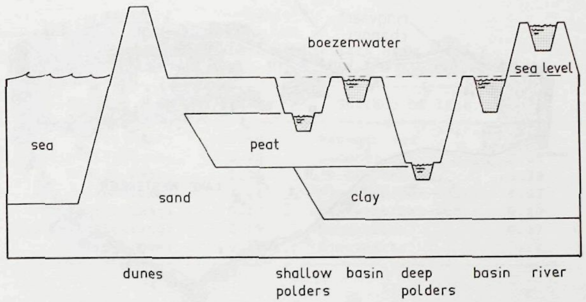


Figure 3: Cross-section of the Netherlands, water-supply and drainage

the most eutrophic part of the Reeuwijk lake area due to the inlet, in dry periods, of water from the bordering Breevaart. In Lake Westeinder, a sediment investigation has been carried out by Paris and Verboon (1974). The aim of that study was an inventory of organic bottom-material in the lake and resulted in maps of the type of sediment material and their locations at that time. Lake Elfhoeven is situated in the south-eastern part of Rijnland. At the time of sampling, phosphate removal experiments were carried out and limnological studies coherent with that were undertaken.

3.2.2 Lake Westeinder

Lake Westeinder, 15 km south-west of Amsterdam, is a eutrophic lake with an average depth of 2.7 m, no deep parts and an area of 9.3 sqkm. The lake is shallow and generally well mixed. Lake Westeinder is described by de Groot (1979) and Schmidt van Dorp (1978). Morphometrical and hydrological data are given in table 1 and a map of the lake is shown in fig 4. The sampling locations, indicated on this map will be discussed in the next section.
The Ringvaart canal of the polder Haarlemmermeer borders the western part of lake Westeinder from Leimuiden-village to Rijsenhout-village. Lake Westeinder is divided in two basins: a large one, the Grote Plas, and a much smaller one, the Kleine Plas.
The lake is used for recreation and sport: the Grote Plas by sailors, windsurfers and swimmers and the Kleine Plas provides quiet harbour places to stay overnight.

The average residence time of the water in the big pool lies between 5 and 10.7 months as discussed in chapter VII.

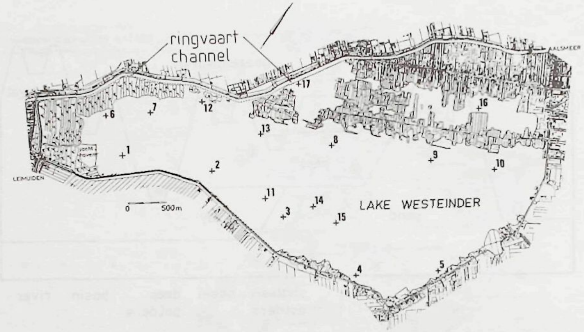


Figure 4: Map of lake Westeinder, the Netherlands

Table 1.

Lake Westeinder: Morphometry and hydrology

East longitude		4 dgr 45 min
North latitude		52 dgr 15 min
Waterdepth	average	2.7 m
	min	1.5 m
	max	3.5 m
level of the balancing system to mean sea level		-0.60 m (average)
watersurface		9.30 km2
length	max	ca. 6000 m
width	max	ca. 2100 m
lake volume		25.11 million m3

3.2.3 Lake Elfhoeven (Reeuwijk lake area)

Lake Elfhoeven is one of a number of interconnected basins in the Reeuwijk lake area, which is part of Polder Reeuwijk, a polder with an area of 27.2 sqkm. The total lake area is about 7.6 sqkm of which lake Elfhoeven covers 1.1 sqkm. The lake area is close to Gouda-city in north-eastern direction and directly eastern to Reeuwijk village. The areas of the *different lakes of the* Reeuwijk lake area that are connected are given in table 2. In figure 5, a detailed map of the Reeuwijk lake area with the connections between the separate lakes is given (Pater, 1981). Morphometrical and hydrological data of lake Elfhoeven are shown in table 3.

Table 2.

Lakes in the Reeuwijk lake area

Surface of lake	[sqkm]	Surface of lake	[sqkm]
Vrijhoef:	0.60	Ravensberg:	1.18
Klein Elfhoeven:	0.26	Sloene:	0.08
Elfhoeven:	1.09	's Gravenkoop:	0.79
's Gravenbroek:	*1.01*	*Nieuwenbroek-oost:*	*0.63*
Klein Vogelenzang:	0.17	Nieuwenbroek-west:	0.40
Groot Vogelenzang:	0.18	Roggebroek:	0.37
Kalverbroek:	0.33	Breevaart:	0.11

3.3 SELECTION OF THE SAMPLING LOCATIONS

In general, a sampling program aims at obtaining reliable information at acceptable costs. When a sampling program is *planned, a statistical conflict arises between (1) the number* of samples required for a good description of the contents in the lake-bottom and (2) the practical restrictions: carrying out a sampling program is expensive.

It is clear that the only way to get a perfect insight in *the contents of the sediment would be to examine the whole* sediment body using a perfect analytical procedure. As this is not realistic, the samples must together feasibly represent the sediment (Ellis, 1980, Ellis and Lacey, 1980). This can be achieved with a network of locations that should be sampled frequently. More samples are more expensive, with *less samples a larger uncertainty must be accepted. The sampling* can in principle be continuous or discrete. Intermittent sampling is the only possible way in sediment sampling. Straight practical answers must now be given for the following questions:

(1) How many samples should be taken to obtain a reliable *picture of the sediment in the lake;*
(2) What sampling locations must be chosen;
(3) To what depth should the sediment be sampled;
(4) What diameter should the sediment cores have;
(5) What disturbance of the core is accepted;
(6) What analyses should be executed.

The specific demands of each research program determine the anwers to these questions. Some additional remarks will be given here sequentially, as well as the decisions taken in in this study:

ad (1) number of samples

More in general, the question of the samplesize is: how many samples from the lake or lake sediment are needed to obtain reliable information. In the general form, this question is hard to answer. The necessary number of samples is dependent on several factors listed in table 4.

Figure 5: Map of Reeuwijk lake area, the Netherlands

To obtain a reasonable view of a population (in this case the concentrations in the sediments) the population mean and standard deviation must be known. As in our case these are unknown, a sample is taken from which these two parameters are estimated. Because no estimation of the standard deviation was available in our study, the way of try and see was adopted: we took a sample consisting of N cores that was expected not to be too small. After analysis, the average x(av) and the standard deviation (s) can be calculated. Whether or not the samplesize was large enough can now be calculated with a method, derived from Elliott (1977) and

Table 3.

Lake Elfhoeven: Morphometry and hydrology

East longitude		4 dgr 45 min
North latitude		52 dgr 2 min
Waterdepth	average	3 m
	min	1.5 m
	max	10.0 m
waterlevel to mean sea level		-2.20 m (average)
watersurface		1.10 km2
length	max	ca. 1200 m
width	max	ca. 1000 m
lakevolume		3.3 million m3

Table 4.

Factors influencing the samplesize

factor of influence	usual situation
(a) dimensions of the area to be investigated	known or can be determined
(b) variation in *composition* of the bottom to be sampled	*unknown*
(c) variation per parameter of the bottom to be sampled	unknown
(d) waterflow in and around the lake	often not fully known
(e) requested accuracy	to be chosen

Southwood (1978). The right samplesize (n) -taking the observed distribution into account- is calculated from the statistics of the actual sample and an accepted error E of the samplemean.

$$n = \frac{(s)^{2}}{[E/100 * x(av)]^{2}}$$

in which:

n = number of cores to be taken, necessary to reach the desired level of accuracy (to be calculated)
s = standard deviation calculated from the results of the sample
E = accepted percentual error in the average
x(av) = average value of the results of the sample

The calculations are done in chapter VIII.

ad (2) sampling locations

The location of the sampling points is dependent on available knowledge. In absence of knowledge a random grid can be applied, when some knowledge is available the sampling locations are determined so-called stratified random. Additional information like knowledge of the waterflow, maps of the lake and surroundings and contacts with people who know the surroundings can reduce the number of samples and influence the choice of the locations to be sampled on. In most cases some preliminary knowledge can be obtained. In this study the maps of the soil-type from Paris and Verboon (1974) are used as criterion to roughly select the sampling locations in lake Westeinder. In many cases, the character of the lake-bottom had changed since then and was different from those maps. Most cores showed brown toplayers and dark brown or black layers underneath, suggesting a more reduced situation than the yellow and brownish sediment layers that were observed by Paris and Verboon.
In lake Elfhoeven sediment-cores were taken from the deep part of the lake, just around this area and on locations spreaded along the rest of the lake. The exact sampling locations are given in the figures 4 and 6.

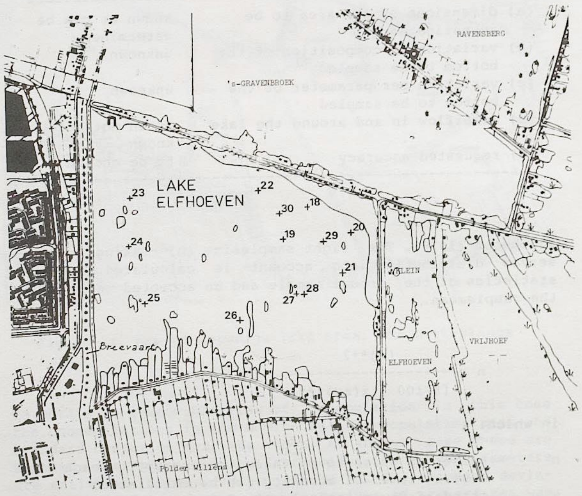


Figure 6: Sampling locations in lake Elfhoeven

ad (3) length of the cores

To decide about the length of the core one has to choose in advance where to put the limits of the system of sediment and water (Tessenow, 1979), dependent on the goals of the investigation. The toplayers of the sediment are in direct contact with the supernatant surface water. Deeper in the sediment interstitial water provides the internal transport and also serves as vertical transport medium due to the flow (upwelling or infiltration). These main processes influence the structure in the sediment. The diameter and length of a sediment core are often determined by available equipment. In this study, sediment cores up to 50 cm length were analysed. The cores taken in the field were 70-85 cm long, the possibly disturbed lower part of the cores was discarded.

ad (4) diameter of the cores

The diameter should not be too small. This demand is more severe when a vertical sediment-profile is desired. Thin slicing followed by chemical analysis is required then.
The thinner the slice, the smaller the sedimentvolume of the sub-samples and the smaller the interstitial water volume is, obtained when some of these sub-samples are squeezed. The ratio to which the bottom is sampled is generally very small: with the use of a coring device with an effective diameter of 0.1 m, taking 10 cores per km2 results in an area-ratio of about one to ten million. Using an apparatus of 0.06 m effective diameter results in a ratio of about one to twenty-eight million; both very large ratios. From this it is clear that the diameter is not too critical in respect to the area-ratio. However, in order to reduce the effects of deformations due to shear forces alongside the tube it is advisable not to take too small diameters. A diameter of about 10 cm serves well in most cases. In this study an apparatus with an inner diameter of 0.11 m was used (Ambuehl, 1969).

ad (5) disturbance of the cores

From ad (3) and ad (4) it is clear that equipment is often a limiting factor in the sampling program. From the literature and from personal communication with investigators it appeared that only a few coring devices provide fairly undisturbed cores. The sample itself can only be called representative when the samples are taken and handled in such a way that the measurements result in values that are the same as those in the sediments at the time of sampling (Walker, 1982). The bottom sediment however is so widely varying, especially in the Dutch delta area, that it is very difficult to obtain undisturbed cores under all circumstances. We managed to obtain undisturbed cores, but in some cases more attempts were required, time consuming and thus expensive. Therefore we developed special equipment adapted for our sediments. This work was done together with Eijkelkamp Equipment for Soil Research, a firm that now commercially sells the equipment. The development is decribed in chapter IX. Results in practice showed, that the apparatus worked in a satisfactory manner. Undisturbed cores were obtained from lake- and riversediments (de Kruijk et al, 1984 and Siebers and Donze, 1984).

ad (6) analyses

What analyses are required is of course fully dependent on the research questions. Analyses can be done in the field or in the laboratory on interstitial water and/or on sediment in wet or dry form. In this study the intact cores were transferred to the laboratory where they were analysed. Analytical procedures are dealt with in chapter IV.

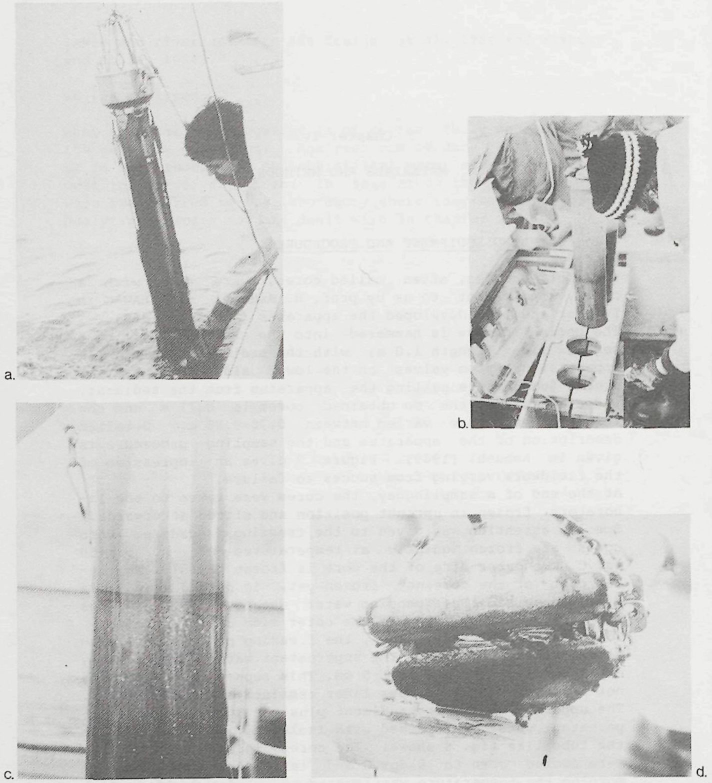
Chapter IV

MATERIALS AND METHODS

4.1 SAMPLING EQUIPMENT AND PROCEDURE

Sediment samples, often called cores, were taken with a corer, kindly lent to us by prof. H. Ambuehl from EAWAG in Switserland, who developed the apparatus (Ambuehl, 1969).
The coring device is hammered into the sediment filling a perspex liner (length 1.0 m) with the sediment sample. The apparatus has two valves on the lower side, that must be closed just before pulling the apparatus from the sediment. The diameter of the so obtained cores is 0.11 m and the length of the core varied between 0.70-0.85 m. Detailed description of the apparatus and the sampling procedure is given in Ambuehl (1969). Figure 7 gives an impression of the fieldwork varying from succes to failure.
At the end of a samplingday, the cores were taken to the laboratory, frozen in upright position and sliced afterwards. Special attention was given to the freezing procedure. When cores are frozen quickly at temperatures of -30 to -50 dgr.C, the outer side of the core is frozen rapidly. The inner part of the core,not frozen yet, is pushed away as a consequence of the expanding water due to frost and rises about 5 cm in comparison to the outer side of the core.
To prevent this disturbance, the freezing process was executed stepwise (fig 8). The supernatant water was carefully siphoned exept for the last 5 cm. This supernatant water was not analysed. The perspex liner remained open at the top. The upper 10 cm of the sediment plus the 5 cm layer of supernatant water was packed with isolating material outside the tube like fig. 8 shows. The cores, in upright position, were cooled down to 0 dgr.C and left overnight. The next morning the temperature was lowered to -1 dgr.C. After 24 h the water surface was frozen. The part of the sediment that was packed remained unfrozen so far. Then, the temperature was lowered to -5 dgr.C and the freezing process of the core proceeded in the way fig. 8 shows. The delay of the freezing of the sediment surface and the toplayers resulted in a frozen, intact sediment surface. Now the temperature was lowered stepwise to -15, -30 and -45 dgr.C every 3 days. Possible further freezing effects were accepted. A samplelength of 50 cm was used for analysis.

In order to saw the cores in one saw cut, a blade with diameter of 30 cm was used, resulting in a loss of material of at least 1.8 mm. Initially, experiments were undertaken to slice the cores with less loss of material. Slicing with a filament (red hot steelwire) was tried. This wire broke again and again, due to sudden local cooling while entering the sediment. No further attempts were made and the loss of



a. fetch up of coring equipment b. tube container c. layered sediment core d. example of a closing failure

Figure 7: Sampling activities on the lakes

1.8 mm material due to the thickness of the circular blade was accepted. In the sawing procedure the thickness of the slices was adapted to this loss, eg. a slice of 5 cm had a thickness of 4.82 cm. No slices thinner than 5 mm (3.2 mm effective) could be acquired this way. When no loss of material is allowed, direct slicing of the wet sediment under *nitrogen-gas can be done (Manning, 1979). No thinner layers* than 2 or 3 mm can be achieved due to rolling up effects of the thin slices. With our samples, that contained small branches, leaves, stones and shells this direct slicing can not be used to obtain thin layers. Particularly in peaty sediments disturbances easily occur. The slicingscheme is shown in fig. 9.

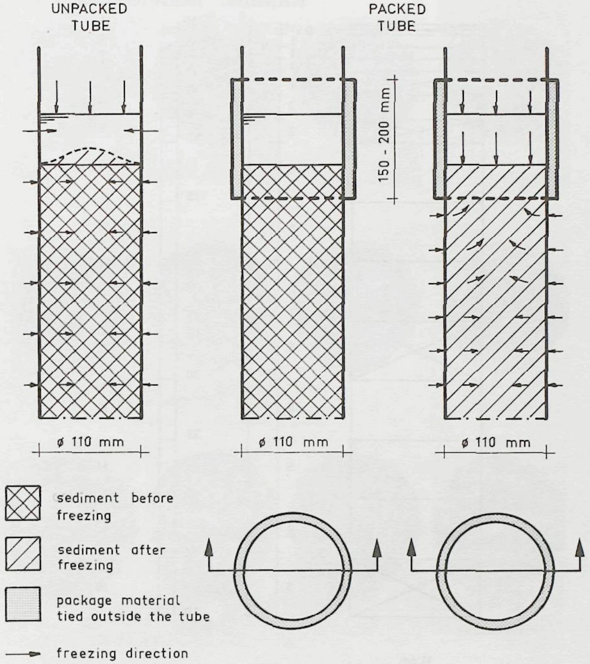


Figure 8: Freezing procedure

16 slices were made, varying in thickness from 0.5 cm (net 0.32 cm) to 5 cm (net 4.82 cm). The slices were coded for

(1) sampling location
 - W = Westeinder
 - R = Reeuwijk (Elfhoeven)

(2) slice number
 - 01 to 16 according to the scheme given in fig. 9.

The slices were photographed and homogenized after thawing by stirring under nitrogen gas in a glove box. The homogeneous material was partly used for sediment analysis, partly for analysis of interstitial water. Stones and branches were removed. *Fig. 10 shows the slices of core 8 (lake* Westeinder) as an example.

Discontinuities in the surface are clear from this figure. It is seen that the sediment surface is not flat (8.1 and 8.2). *In layers 8.4, 8.5 and 8.6 a stone was included in the* core. In layer 8.8 (10 cm depth) shells are visible. Also small branches and roots are seen (slices 8.12 and 8.14).

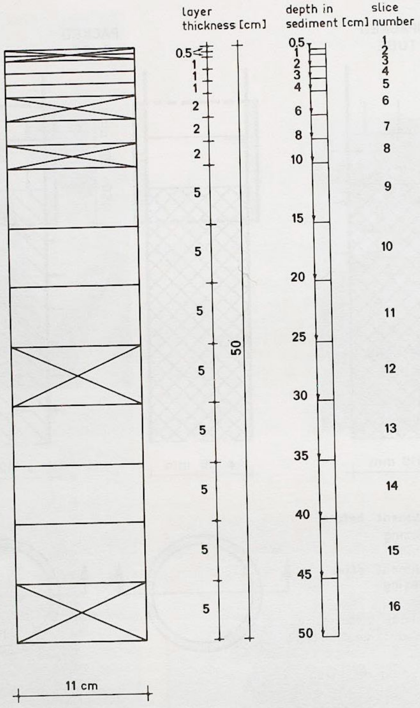


Figure 9: Slicing scheme for the frozen cores

5 slices of each core were analysed (marked with a cross in fig 10) with numbers 01, 06, 08, 12 and 16, representing the sediment depths 0-1 cm, 4-6 cm, 8-10 cm, 25-30 cm and 45-50 cm resp. The interstitial water was obtained by squeezing part of the sediment sample under nitrogen gas (Lyons, 1979), using Sartorius pressure filter equipment (Holland,1977) and Sartorius cellulose-acetate P-free filters (0.45 mu m) and was analysed for ortho-phosphate and total-phosphate, using a Technicon Auto Analyser.

The other part of the sediment was dried using a standard method (NEN 3235, Dutch Standard), the watercontent of the sediment was calculated and all other data were obtained from XRF-Spectroscopic analysis of the dried sediments.

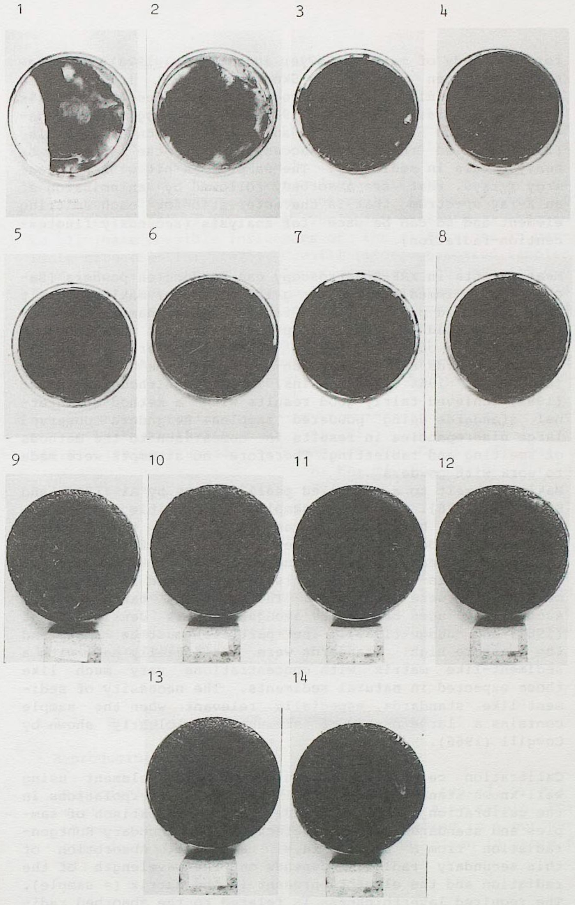


Figure 10: Examples of sediment slices of core 8

4.2 XRF-SPECTROSCOPY

4.2.1 Introduction

XRF-Spectroscopy is a multi-element analysing technique that gives the opportunity to measure several elements in the same sample (Herglotz and Birks, 1978). It is often used for the study of metals (Sawyer and McCarty, 1978). Good results have been reported by Skogerboe (1975) if the sample thickness is uniform. The method is recommended for analysis of solid samples by Steeman (1982). From geological application Reijnders (1964) gives an example. Hahn and Scholer (1983) applied the method succesfully for the analysis of heavy metals in sediments. The sample is hit with high-energy X-rays, that are absorbed, followed by an emission of an X-ray spectrum that is characteristic for each emitting element and so can be used for analysis (secundary fluorescention-radiation).

Measurements in XRF-Spectroscopy can be done on powders (Sacha, 1981) -immediately after grinding, after making a smelt to a so called pearl or after tabletting the sample. Analysis on powdered samples will provide reliable results only when the size of the particles does not differ too much and when standards are used which resemble the used samples (Hautecler, 1964 and Jenkins, 1977). Although Kliment (1981) achieved fairly good results with a method of internal standards using powdered samples, Reijnders observed large discrepancies in results in comparison to the methods of smelting and tabletting. Therefore no attempts were made to work with powders.
Making a smelt to a so called pearl is done by Al (1977) and Kruidhof (1978). With peaty samples, a possible loss of material at the high temperatures can diminish the recovery. The samples from lake Westeinder, and those of lake Elfhoeven are very peaty: branches and roots occur till depths of 50 cm. For this reason no pearls were made and all dry sediment samples were tabletted. The method of tabletting was succesfully used before by amongst others Jenkins et al (1966) and Judge (1980). The particles must be small and the pressure high. Standards were artificially made with a sediment-like matrix with concentrations very much like those expected in natural sediments. The necessity of sediment-like standards, especially relevant when the sample contains a large number of elements, was clearly shown by Cowgill (1966).

Calibration curves were measured for every element using well-known standards (Zwemer, 1982). Only interpolations in the calibration curves were made. A good comparison of samples and standards requires detection of secundary Rontgen-radiation from a uniform layer thickness. Absorbtion of this secundary radiation depends on the wavelength of the radiation and the elements present in the matrix (= sample). The required layerthickness is related to the absorbed radiation and is called the effective layerthickness. Measurements with long wavelengths (the lighter elements) do not cause any problems in this respect, absorption only occurs in thin layers. For many heavy elements however absorption requires a thicker layer. The effective layer for the elements Sn, Cd, Ag and Mo was 1.75, 1.53, 1.40 and 0.60 cm respectively. Especially in the waterrich toplayers of the sediment not enough material was available to produce these thick tablets. Therefore these elements could not be measured. This limitation of the method was reported earlier by Laitinen (1975).

4.2.2 Procedure XRF-Spectroscopy

After drying, the sediment was grinded with a Fritsch P2 Laboratory Planetary Mill with two 80 ml agate bowls or a Fritsch P0 Electromagnetic Laboratory Micro-Pulveriser with a hardmetal tungsten carbide mortar and ball to particles with dimensions varying from 1 - 10 mu m.
The samples were homogenised and tabletted to diameters of 32 mm under 293 MPa and 13 mm under 517 MPa -the latter if little material was available. The high pressure is assumed to eliminate possible influences of the differences in particle-size (Bertin, 1975). Cowgill (1966) prepared samples from lake sediment under a lower pressure: 103 MPa (15,000 lb/sqinch) but longer: for 5 min. Measurements in this study were done with Philips PW 1140/90 equipment with a Rhodium-tube in the Department of Metallurgy at the Delft Unversity of Technology, using an instrument setting of 40 kV and 60 mA. The measurements were corrected for background. The analysing crystals are given below:

PE	Penta-erythritol	Al, Si
LiF200	Lithium-Fluoride	As, Ca, Co, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb, Se, Sr, Ti, Zn
TlAP	Thallium Acid Phtalate	Mg

Detection limits, as calculated for our measurements are given in table 5. The detection limit is calculated in % of the element concentration as the ratio of 2.5 times the square root of the background intensity (Bertin, 1975 and Jenkins, 1977) and the intensity per % of the element. This detection limit is determined for each separate element and is shown in table 5.

4.2.3 Errors in the XRF-Spectroscopy procedure

- Reproducibility

Reproducibility of the XRF-procedure was tested by measuring several elements 10 times on the same sample. For three elements, Fe, Ca and Si, this resulted in a percentual deviation of the average counting, given in table 6 of:

$$\text{Error} = \frac{s}{x(av)} * 100\ \%$$

- Background

The error caused by background counts in the analytical procedure was estimated as the percentual ratio of the standard deviation of 10 backgroundcounts on both sides on 10 tablets per element and the average countings per

Table 5.

Detection limits of XRF-Spectroscopy

element	pellet 32 mm [% of dry wt.]	pellet 13 mm [% of dry wt.]
Al	0.05	0.05 *
As	0.0003	0.002
Ca	0.004	0.017
Cr	0.001	0.001
Co	0.0005	0.002
Cu	0.0004	0.003
Fe	0.004	0.008
Pb	0.005	0.027
Mg	0.017	0.016 *
Mn	0.001	0.006
Hg	0.002	0.005
Ni	0.0003	0.001
P	0.002	0.01
K	0.004	0.012
Se	0.0003	0.001
Si	0.01	0.03
Sr	0.0004	0.002
Ti	0.001	0.005
Zn	0.001	0.004

* measured with tungsten-mask

element:

$$\text{Error} = \frac{s(bg)}{[x(av)]\text{elem E}} * 100 \%$$

This resulted in errors given in table 6.

- Heterogeneities within the sample

Samples were very well homogenized by mixing and grinding, in order to restrict the error caused by subsampling in a probably heterogeneous sedimentsample. This error was calculated as the percentual deviation of the average value of the counts on 10 tablets (both sides counted) made out of one grinded and homogenized sediment sample. Standards were measured at the beginning, during and at the end of every measuring series.

Table 6.

Errors in the XRF analytical procedure

	Fe [%]	Ca [%]	Si [%]
Reproducibility	0.16	0.12	0.60
Background	0.01	0.01	0.04
Heterogeneities	1.59	1.62	3.42
Maximum error	1.76	1.75	4.06

4.3 DETERMINATION OF PHOSPHATES

4.3.1 Determination of ortho- and total-phosphate

The squeezed interstitial water phosphate was analysed colorimetrically according to Lennox (1979), adapted for our Technicon Auto Analyser. Destruction before analysing the total-phosphate was according to Technicon in strong acid environment.

4.3.2 Determination of phosphate in solid sediment

Destruction of the sediment before analysing the total-phosphate was done with a modified Technicon method in strong acid environment. The sediment material is heated before it is placed in the destruction block in order to avoid poor contact between acid and sediment in the first phase of the destruction. With this pretreatment, problems with splashing of material during the destruction process were reduced. In peaty sediments special problems can arise, because quite often the sediment does not dissolve completely. This can result in a decreasing recovery, but the deviations are unknown and may vary widely. The destruction method for P-analysis of the sediment was therefore tested by hydrogen-fluoride treatment on the residues and standard addition method. The additions were all recovered and it appeared that the residues of the loamy-type sediments contained 1.2 % and those of peaty sediments 2.9 % of the phosphate concentrations of the samples.

Chapter V

THREE-DIMENSIONAL DISTRIBUTION OF THE ELEMENTS IN THE LAKESEDIMENTS

5.1 INTRODUCTION

Thirty cores were taken from the sediments, 17 from lake Westeinder and 13 from lake Elfhoeven. The cores were sliced (fig. 9) and subsamples of 5 slices, representing five depths in the sediments, were chemically analysed. These depths are: 0-1 cm, 4-6 cm, 8-10 cm, 25-30 cm and 45-50 cm. The concentrations are expressed as percentage of the dry weight of the sediment. The average concentration and the standard deviations were calculated for both lakes and for each of the five depths in the sediment. On 16 sediment depths the concentration of phosphate in the sediment and the ortho- and total-phosphate concentration of the interstitial water was determined.

The distribution of the mentioned concentrations of 20 elements, including heavy metals, in the sediments of lake Westeinder and lake Elfhoeven is discussed in chapter X. When variability is observed this can lead to recognition of patterns. The concentrations are also compared to those, measured in other lake- and riversediments. Literature was obtained with techniques, described in Siebers and de Jong-Hofman (1983).

Inspection of the data (chapter X) showed that in most cases the data show little structure. The surface area of the samples taken in the two lakes is only a small part of the total area of the lakebed and it thus can be asked whether the sample is representative for the whole lake. A more representative sample can be achieved by taking more samples or taking samples with a larger surface area. Apart from the practical consequences, it is questionable whether samples with a diameter of for instance 1 meter increase the quality of the sample. From the observations it appeared, that two cores, taken within a few meters from each other can show contents, that differ up to a factor 10. The dominating scatter thus is present on a scale of a few meters. An example can be given for the element arsenic: on a depth of 0-1 cm, the content in cores 27 and 28, two cores taken at a distance of a few meters are 0.001 % and 0.013 % arsenic.

A large diameter core with technically reasonable dimensions (0.40-0.50 m diameter) thus is no guarantee that those extremes will be detected. It may be wiser to take two or three samples on locations close together and mix the subsamples. This can be done for the depth-layer, from which the information is required. This method does not guarantee the detection of the observed differences either, but sampling several square meters of the sediments is far too costly. Taking three cores on 'one' sampling location is already expensive and time-demanding but it is about the minimum required for reliable results.

In the absence of knowledge of three-dimensional structure we can first attempt a statistical analysis of the data to gain a better insight and to increase our view about possible relations that exist. This is done below. We tried to get some knowledge from a statistical look upon the data. First, the average concentration of the elements in the whole 50 cm thick sediment layer, the standard deviations of the sample and the standard deviation as percentage of the mean are shown in table 7.
The figure of the average concentration is calculated as the arithmetic average of the measured concentrations at 5 depths in the sediment core and is therefore not the exact value that can only be calculated by mixing the whole 50 cm thick layer. This was not done because of the desired distinction in depth structure of the sediment.

Next, all measured element concentrations were correlated pairwise. The 1 % significant correlation coefficients for both lake Westeinder as lake Elfhoeven were put in a matrix. This matrix is shown in table 8. From this table it appears that elements that belong to the same group of the periodic table of elements show different results. This is the case with for example phosphorus and arsenic that show large differences in correlation coefficients. Their correlation to aluminum, calcium and iron is of special interest. The observed differences between phosphorus and arsenic are also in contradiction with our findings in the sediments in the Andelse Maas Basin (the Netherlands), where we observed strong correlations between iron and phosphorus (r=0.91) and iron and arsenic (r=0.91) in the toplayers (de Kruijk et al, 1984). As it was considered that the large quantity of data, 71 and 62 pairs of observations for lake Westeinder and lake Elfhoeven sediments resp., can hide structures, it was tried to discover indications of structures from the statistical correlation of data from the same depth of the sediment. This, however, did not give more insight.
In view of the existing literature on these chemicals (mainly P, Fe, Ca and Al) it is surprising that we could not detect strong correlation in the data from the field.

It is concluded that for some elements like arsenic a strong scatter was observed and no structure could be traced as for other elements, which were also widely scattered, clear structures could be established. This is the case with phosphate and copper.

From this simple statistical treatment of the data it can be concluded that the mechanisms that have led to the observed scatter are probably different and a poor correlation between the elements exists. Observed patterns can lead us further only then when it is located on a scale on which the measurements have been done. The first hypothesis then is that the concentration is dependant of depth. Horizontal structures are far more difficult because they only can be recognized when some knowledge about the vertical pattern is already available. A high standard deviation can be indicative for such geometrical patterns, that exist as a consequence of still unknown processes. Recognition is important because patterns increase the scatter. The processes that are involved are concentration mechanisms and dispersion mechanisms. These mechanisms probably have strong variable characteristics that make their outcome unpredictable. Some remarks can be made on this.

Table 7.

Mean concentrations and standard deviations

Mean concentrations and standard deviations [sd] of the sample and the percentual standard deviations in a 50 cm thick sediment layer in lakes Westeinder and Elfhoeven.

	lake Westeinder			lake Elfhoeven		
	mean	sd	sd as % of mean	mean	sd	sd as % of mean
	[% of dry weight]			[% of dry weight]		
Al	0.9	0.7	78	2.1	0.7	33
As	0.002	0.002	100	0.003	0.003	100
Ca	11.6	5.3	46	7.9	1.2	15
Cr	0.023	0.005	22	0.027	0.002	7
Co	0.003	0.002	67	0.005	0.002	40
Cu	0.014	0.015	107	0.010	0.006	60
Fe	2.45	1.14	47	3.39	0.62	18
K	1.2	0.4	33	1.6	0.4	25
Mg	0.08	0.09	113	0.234	0.116	50
Mn	0.21	0.11	52	0.11	0.03	27
Ni	0.002	0.001	50	0.003	0.001	33
P	0.082	0.050	61	0.084	0.031	37
Pb	0.01	0.009	90	0.021	0.024	114
Si	22.6	6.6	29	24.9	4.5	18
Sr	0.047	0.011	23	0.043	0.006	14
Ti	0.05	0.05	100	0.11	0.03	27
Zn	0.021	0.018	86	0.021	0.014	67
Interstitial water in [mgP/l]						
oPO4	2.08	2.32	112	0.50	0.50	100
tP	3.27	3.34	102	1.11	0.97	87
Watercontent in [%]						
	84.4	12.7	15	83.8	7.9	9

If the observed standard deviations are large in comparison to the mean, concentration mechanisms predominate and local accumulations of that element in the sediment can be expected. If the influence of the concentration mechanisms is

Table 8.

Correlation matrix for average sediment concentrations

	AL	AS	CA	CO	CR	CU	FE	K	MG	MN	NI	P	OPO4	TPO4	PB	SI	SR	TI	ZN	H20
AL				.36			.47	.72	.39		.46					.50	-.42	.75		
AS																				
CA				-.37		.32	-.52	-.37	-.58	-.31		.31					.72	-.52		
CO	.59	.40					.84	.51	.39	.48	.73							.64	.35	
CR	.39			.33											.46					
CU					.65		.33								-.36	.37				
FE	.58			.84	.45			.57	.57	.50	.78				.41		.35	.81		
K	.61		.46	.63			.56		.63		.50					.65	.65	.82		.45
MG	.59		.34	.56		-.42	.41	.70			.42						.42	.71		
MN				.42		-.33			.39		.49	.35			.54	-.53			.57	.40
NI	.68			.89	.36		.84	.71	.57	.33		.61	.31		.51			.65	.58	
P	.59		.34	.53	.56		.59	.41			.62								.47	.51
OPO4						-.41		.38	.46					.67	.43				.46	
TPO4								.40	.41				.59				.33		.67	
PB																			.71	
SI	.61		.58	.39	.40			.81	.49		.49	.47					-.55			.74
SR	.54		-.35	-.48			.37	.79	-.52		-.52	-.37				-.84		-.50		.55
TI	.73			.67	.62		.77	.58	.41		.71	.76				.61	-.54			
ZN				.40		.34		.48		.43	.55									
H20					.40	.39		-.49	-.44				-.40	-.36		-.37	.37			

LAKE WESTEINDER

LAKE ELFHOEVEN

small or absent, the dispersion mechanisms are predominant and on the long run the concentrations will be equal all over the area resulting in lower values of the standard deviation. Moreover, some dispersion mechanisms, like bioturbation are not selective for elements and locations while concentration mechanisms as for instance chemical reactions are. If they were not, then all accumulations would have been found on the same (few) location(s), which is certainly not the case. This is illustrated by table 8.

Increasing dispersive activity can result in decreasing correlation coefficients between the elements in the lakesediments. Concentration mechanisms are assumed to differ for every element. If (some of) these processes are the same for two elements, this coincidence will increase the correlation that exists between these two elements. In first approximation it can be expected, that a higher correlation between two elements originates from more common concentration mechanisms for those elements. Also in first approximation it is assumed that if the correlation is not significant, the elements are not related to each other. For the statistical discussion, bioturbation does not explain the difference in standard deviation, as a consequence.

From table 8 it appears to be possible to discuss some differences between the two lakes under investigation. It it not possible however to directly trace mechanisms with these correlations One has to be careful with this. This is also reported by Boust et al (1981). In some respect, it shows the way to future research. Dispersion will become smaller with depth due to the reducing bioturbation. In fact, all processes will reduce with depth exept for processes, that are dominated by infiltration.

The concentration mechanisms are mostly selective on one or some elements. For chromium, the result is a very uniformly distributed concentration, thus suggesting either equilibrium or a small influence of the concentration mechanisms on chromium. Further investigations should be aimed however on the concentrations mechanisms that caused the high variability of the elements arsenic and lead and also of the concentrations total- and ortho-phosphate in the interstitial water of the sediment. From the observed high three-dimensional variability the largest possible effect can be expected. Unfortunately we lack the knowledge of these mechanisms, but experiments can be done, especially with the latter elements.

If for instance 5 elements are significantly different between the two lakes, this can be due -next to causes like inputs- to differences in dispersion- and concentration mechanisms, other causes like inputs held constant. It is not yet possible to split these mechanisms. If more detailed information is required, more data should be available. If a limited dataset is available as is often the case , the methods to deal with are more coarse and less precision must be accepted in order to discover more structure. In chapters VI and VII the structures that were observed in the copper- and phosphate data are discussed. In this chapter the occurrence of patterns in the distribution of the elements is disregarded and the statistical properties of the data are used to compare and arrange the elements with respect to their distribution in the lake-bottom and for their distribution with depth in the sediments. These distributions are expressed as factors of inhomogeneity: horizontally (symbol: HI) and vertically (symbol: VI).

Distinction between elements with statistical distribution and elements with a distribution pattern can lead to one step more insight in existing structures. These structures need further evaluation. Analysis of our observations thus leads to a multitude of questions that we could not pursue on the basis of existing data but that may allow starting points for new research.

5.2 INPUTS AND TRANSPORT PROCESSES

Attempts to interpret differences in the data of the sediments with the help of geological and topographical maps of the surrounding soil did again not result in correlations between the lake bottom and the soil in the surrounding polders.
Data of natural background concentrations of eroding, calcium-rich rock in the river Rhine and measured concentrations in the Rhine (Schuiling, 1974, Scholte Ubing, 1980 and the yearly reports of the International Consortium of Water Sup-

ply Undertakings in the Rhine Catchment Area -in dutch: Rijncommissie Waterleidingbedrijven-) indicate, that metal concentrations in the Rhine water followed the increasing and reduced discharges in the last ten years. Transport of erosion products from the catchment area of the Rhine can also lead to enrichments in the araes downstream. Some elements are bound to sediments more rapidly and in more stable forms than others or dependent on the chemical environment, pH, etc. (Foerstner and Salomons, 1983). Between 1960 and 1970 the history of the Rhine sediments indicates a decreasing content for arsenic, zinc, lead and antimony and an increase for copper, chromium, mercury, nickel and cadmium (de Groot and Allersma, 1975 and Salomons and Forstner, 1984). From 1970 to 1980 chromium and cobalt increased again, nickel, cadmium and zinc remained about constant and lead, copper, arsenic and mercury decreased (Salomons and Forstner, 1984).

De Groot and Allersma stated that cadmium appeared to be one of the elements with a large ratio [metal in water/metal in sediment], which suggests transport through the water mainly. The cadmiumcontent of the Rhine water however decreased stepwise from 3 ppm to 0.9 ppm Cd in the time period 1960-1970 while the cadmium content of the Rhine sediment increased with a factor 1.94 in the same period.
Only a complete inventory of all inputs in the whole catchment area as well as knowledge of the concentrations along the river length, in fact a mass balance per element, allows reliable quantitative calculations. This subject needs further research and can be most effectively approached by first making mass balances of only those elements, that show structure in composition.

The observed variability in the sediments is the result of several transport processes in the lake. Some of them are:

(1) exchange processes at the sediment-water interface
(2) distribution and redistribution of natural inputs and contents
(3) hydrological and geohydrological processes (waterflow on and below the land and sediment surface)
(4) distribution of inputs on the waterinflow from polders and boezemwater
(5) distribution of diffusive inputs from the shores and from boats (mainly recreational activities)

Inputs into the system of lakewater and sediments together with the sum of the processes in the system result in the observed data. The processes will not be evaluated here, but some remarks can be made. When an element is discharged on a lake from whatever source, two important processes determine the fate of the input: (1) the mixing characteristics of the water body and (2) the sorption characteristics of the sediment. Driving forces can be sedimentation, downward percolation, differences in pH and sedimentation of algal material. Differences between the sediments in the lake and in the canal can also partly be caused by this.

Two extreme situations can be distinguished. When, the time constants of the processes considered, mixing of the lakewater is far more important than the binding processes, an input of an element is rapidly spreaded over the whole lake area. This is reflected in a uniform concentration pattern in the water and probably also in the sediments. This is the case under assumptions of homogeneity of composition and adsorption capacity of the bottom.

The other extreme situation occurs when the sorption processes of the elements into/onto the sediment are much faster than mixing of the water. This results in high local concentrations. These two extremes and the situations inbetween are shown in figure 11, a schematic representation of the situation in the lake that follows the input of an element. As differences in local binding capacity of the sediment occur, the scheme will in fact be far more complicated.
The inputs can thus be processed as follows: (1) Poor mixing and fast binding processes (2) Poor mixing and slow binding processes (3) Rapid mixing and fast binding processes (4) Rapid mixing and slow binding processes

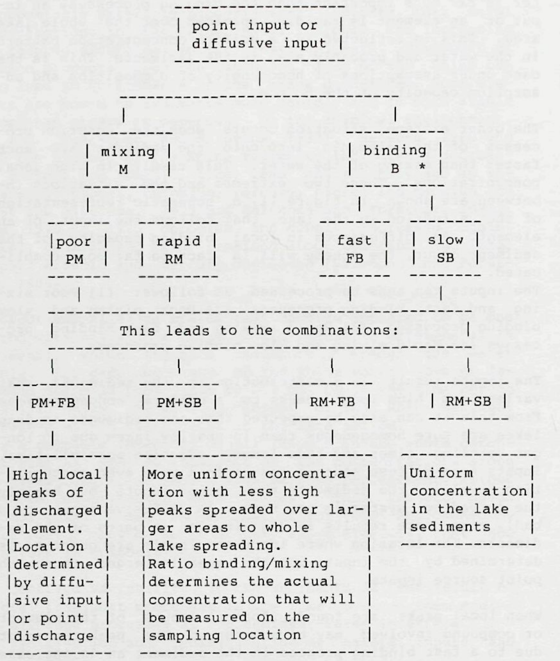
The inputs result in a distribution in the sediments, that varies from high local peaks to a uniform concentration. From this it can also be expected that the sediments in deep lakes are more homogeneous than in shallow lakes due to longer settling times and thus longer reaction possibilities. Inputs from diffuse sources result in a more even concentration-level in the sediments than point inputs but basicly the spreading system is the same. A diffusive input on a badly mixed lake results in high levels in parts of the sediments. The location where increased levels are observed is determined by the input, but the area is larger than with point source inputs.

When local peaks are found, (former) inputs of the element or compound involved may have occurred. The peak can exist due to a fast binding process in the sediment as is the case with copper in lake Westeinder sediments (chapter VI) and/or poor mixing of the water mass in the lake. The input can be composed from natural background and inputs. In absence of inputs, local differences can be attributed to, for instance geographical differences (Reynoldsen, 1982). In most cases the required information on the three-dimensional distribution of the elements is lacking. We therefore tried to arrange the elements for their observed variability.

5.3 HORIZONTAL VARIABILITY OF THE ELEMENTS

5.3.1 Calculation method for horizontal inhomogeneity

The horizontal inhomogeneity of the elements with symbol HI, is defined as the ratio of the range and the average value of the observations. HI is calculated for the five sediment depths wherefrom samples were analysed. The range is the



High local peaks of discharged element. Location determined by diffusive input or point discharge

More uniform concentration with less high peaks spreaded over larger areas to whole lake spreading. Ratio binding/mixing determines the actual concentration that will be measured on the sampling location

Uniform concentration in the lake sediments

* One average binding capacity of the sediment is assumed, for reasons of simplicity. A differentiated binding in fact is necessary.

Figure 11: Effect of inputs on the observed concentrations in the sediments

maximum minus minimum content in that layer.

$$HI = \frac{c(max) - c(min)}{c(aver)} = \frac{range}{c(aver)}$$

The value HI is zero when the variation within the horizontal layer is extremely small or zero. An increasing variability of the elements within the sedimentlayer in the lake increases the value of HI. The range of the observations is used as measure for the variability instead of the standard deviation of the observations because we wanted to compare

the horizontal and vertical variability. In vertical direction analyses were done only on five depths and application of the standard deviation is not meaningful then.

5.3.2 Results and discussion

Table 9.

Horizontal Inhomogeneity in lake Westeinder sediments

the code W = Lake Westeinder,
the slicenumbers 01 to 16 represent depths (fig. 9)

slice	W 01	W 06	W 08	W 12	W 16	W av
depth cm	0-1	4-6	8-10	25-30	45-50	0-50
Al	2.13	1.40	1.31	4.29	4.75	3.89
As	3.00	2.67	2.33	2.50	4.67	7.00
Ca	1.21	1.29	1.28	1.69	1.68	2.01
Co	4.00	2.33	2.33	2.00	2.50	2.67
Cr	0.35	0.35	0.50	0.48	1.20	1.39
Cu	1.94	1.62	1.46	0.43	0.71	5.43
Fe	1.52	1.89	1.61	1.11	1.61	1.85
K	0.74	1.09	0.63	1.85	2.60	2.38
Mg	8.00	2.46	1.93	3.91	3.69	4.93
Mn	1.87	1.86	2.02	1.17	1.43	2.26
Ni	2.00	2.00	2.00	2.00	3.00	2.00
P	1.27	1.95	1.76	3.43	1.54	3.23
Pb	6.75	3.10	2.57	2.00	2.18	3.60
Si	0.89	1.18	0.73	1.20	1.56	1.35
Sr	0.86	0.78	0.79	0.93	1.05	1.21
Ti	2.86	2.65	2.39	3.77	4.88	4.67
Zn	3.59	3.10	2.82	2.19	2.77	3.76
oPw	1.83	3.14	4.24	4.22	3.18	6.12
tPw	2.33	2.94	3.43	4.84	4.63	4.89
H20	0.48	0.77	0.70	0.47	0.46	0.79

From tables 9 (Westeinder) and 10 (Elfhoeven) the variability per element as defined by HI can be read. Some remarks can be made on this.

Al The horizontal heterogeneity in the toplayer is higher than between 4 and 10 cm. Deeper in the sediment an increase of the horizontal inhomogeneity occurs in both lakes.

As The horizontal inhomogeneity of arsenic is high at all depths. In the toplayer and in the deepest layer, the largest heterogeneities is observed in both lakes.

Table 10.

Horizontal Inhomogeneity in lake Elfhoeven sediments

the code R = Lake Elfhoeven (Reeuwijk lake area),
the slicenumbers 01 to 16 represent depths (fig. 9)

slice	R 01	R 06	R 08	R 12	R 16	R av
depth cm	0-1	4-6	8-10	25-30	45-50	0-50
Al	1.25	0.73	0.81	1.14	1.57	1.75
As	4.33	2.00	1.67	2.33	3.67	4.33
Ca	0.22	0.25	0.37	0.74	0.63	0.79
Co	1.40	1.00	1.20	1.50	1.50	1.60
Cr	0.23	0.15	0.11	0.07	0.27	0.48
Cu	1.10	0.75	1.70	0.75	0.75	2.90
Fe	0.36	0.72	0.60	0.58	1.11	1.09
K	0.21	0.49	0.60	1.06	1.55	1.40
Mg	2.95	0.98	0.98	1.28	1.70	2.24
Mn	1.26	0.74	0.56	0.65	0.87	1.19
Ni	0.67	1.00	0.67	1.00	1.33	1.33
P	0.60	0.93	0.58	1.06	1.11	1.45
Pb	6.38	4.70	0.91	4.71	1.68	7.33
Si	0.28	0.30	0.25	0.80	0.99	0.87
Sr	0.19	0.17	0.20	0.64	0.89	1.07
Ti	0.50	0.82	0.81	1.01	1.33	1.60
Zn	3.00	0.96	1.15	3.00	1.90	3.86
oPw	3.04	5.36	3.58	3.09	2.28	4.69
tPw	2.65	3.40	2.99	1.98	1.85	4.07
H2O	0.17	0.33	0.26	0.32	0.35	0.40

Ca	Calcium in lake Elfhoeven is more even than in lake Westeinder sediments. The heterogeneity increases with depth.
Co	A large horizontal inhomogeneity occurs in the toplayer of lake Westeinder. In deeper layers in lake Westeinder and on all depths in lake Elfhoeven sediments the variability in horizontal inhomogeneity is only small.
Cr	Chromium is very uniform in both lakes at all depths.
Cu	Horizontal heterogeneity in the toplayers is large.
Fe	The inhomogeneity in the toplayer of lake Elfhoeven is low in comparison to deeper layers. In lake Westeinder, the horizontal inhomogeneity is about the same at all depths.
K	The horizontal inhomogeneity increases with depth in both lakes.
Mg	The horizontal inhomogeneity in the toplayer of 1 cm thickness is extremely high. Between 2-10 cm the horizontal inhomogeneity is decreasing and in layers deeper than 10 cm increasing again. This is the case for both sediments.
Mn	The horizontal inhomogeneity in the upper 1 cm (Elfhoeven sediments) and in the upper layer of 10 cm (Westeinder) is higher than in the deeper layers.
Ni	Nickel is fairly uniform with depth in both lakes.

P	The horizontal inhomogeneity is about the same at all depths.
Pb	The horizontal inhomogeneity is high, especially in the toplayers both lakes. In the layer 8-10 cm it is somewhat lower.
Si	In the toplayer of lake Elfhoeven sediments the horizontal inhomogeneity is lower than that in deeper layers. In lake Westeinder, a fairly uniform distribution of silicon with depth is observed.
Sr	In the toplayer of lake Elfhoeven a lower horizontal inhomogeneity is observed than in deeper layers. In lake Westeinder a fairly uniform distribution in vertical direction is observed.
Ti	In lake Elfhoeven the layer 0-1 cm shows a low horizontal inhomogeneity, deeper in the sediment an increasing heterogeneity is observed. In lake Westeinder, a much higher horizontal inhomogeneity, especially in deep layers is shown.
Zn	In lake Westeinder, the largest variations are observed in the toplayers. In lake Elfhoeven, the smallest horizontal inhomogeneity occurred in the layer just below the toplayer.
oPw	and tPw The ortho- and total-phosphate concentrations in the interstitial water of the sediments are very variable at all depths in the sediments of both lakes. They belong to the most scattered concentrations measured in the sediments.
H2O	Watercontent of the sediments is rather constant in horizontal direction in both lakesediments.

From tables 9 and 10, a rank order can be made for the elements, from most varying element to least varying element by sorting the HI values per horizontal layer in the sediments. This results in table 11 that is discussed next.

Lake Westeinder

In the toplayer of the sediments magnesium and lead are by far the most varying elements with HI-factors as high as 8.00 and 6.75. The contents of inorganic phosphate and total phosphate in the interstitial water also vary widely in all horizontal layers. The sequence of variation of the elements is by no means the same in all horizontal layers. In the toplayer the variations are larger than in the deeper layers of the sediment. Only with the elements lead and copper, the horizontal inhomogeneity decreases with depth. An increase of the variation with depth is shown by chromium. The rest of the elements show scattered views in respect to the structure with depth or are fairly constant (Si and Ni).

Lake Elfhoeven

The factors of inhomogeneity are of the same order as in lake Westeinder. Lead and ortho-phosphate are the most varying elements in the layers between 0 and 30 cm in lake Elfhoeven sediments, arsenic in the deepest sediment layer (45-50 cm). The variation of ortho- and total-phosphate concentrations is large at all depths in the sediments. Some remarks are given for some elements arranged according to their position in the periodic table of elements.

Table 11.

Rank order of horizontal inhomogeneity in both lake-sediments

Rank order in lake Westeinder (W) and lake Elfhoeven (R) for five depths in the sediments and for the average (50 cm)

0-1 cm	4-6 cm	8-10 cm	25-30 cm	45-50 cm	0-50 cm
HI	HI	HI	HI	HI	HI
W 01	W 06	W 08	W 12	W 16	W av
Mg 8.00	oPw 3.14	oPw 4.24	tPw 4.84	Ti 4.88	As 7.00
Pb 6.75	Pb 3.10	tPw 3.43	Al 4.29	Al 4.75	oPw 6.12
Co 4.00	Zn 3.10	Zn 2.82	oPw 4.22	As 4.67	Cu 5.43
Zn 3.59	tPw 2.94	Pb 2.57	Mg 3.91	tPw 4.63	Mg 4.93
As 3.00	As 2.67	Ti 2.39	Ti 3.77	Mg 3.69	tPw 4.89
Ti 2.86	Ti 2.65	Co 2.33	P 3.43	oPw 3.18	Ti 4.67
tPw 2.33	Mg 2.46	As 2.33	As 2.50	Ni 3.00	Al 3.89
Al 2.13	Co 2.33	Mn 2.02	Zn 2.19	Zn 2.77	Zn 3.76
Ni 2.00	Ni 2.00	Ni 2.00	Co 2.00	K 2.60	Pb 3.60
Cu 1.94	P 1.95	Mg 1.93	Ni 2.00	Co 2.50	P 3.23
Mn 1.87	Fe 1.89	P 1.76	Pb 2.00	Pb 2.18	Co 2.67
oPw 1.83	Mn 1.86	Fe 1.61	K 1.85	Ca 1.68	K 2.38
Fe 1.52	Cu 1.62	Cu 1.46	Ca 1.69	Fe 1.61	Mn 2.26
P 1.27	Al 1.40	Al 1.31	Si 1.20	Si 1.56	Ca 2.01
Ca 1.21	Ca 1.29	Ca 1.28	Mn 1.17	P 1.54	Ni 2.00
Si 0.89	Si 1.18	Sr 0.79	Fe 1.11	Mn 1.43	Fe 1.85
Sr 0.85	K 1.09	Si 0.73	Sr 0.93	Cr 1.20	Cr 1.39
K 0.74	Sr 0.78	K 0.63	Cr 0.48	Sr 1.05	Si 1.35
Cr 0.35	Cr 0.35	Cr 0.50	Cu 0.43	Cu 0.71	Sr 1.21
R 01	R 06	R 08	R 12	R 16	R av
Pb 6.38	oPw 5.36	oPw 3.58	Pb 4.71	As 3.67	Pb 7.33
As 4.33	Pb 4.70	tPw 2.99	oPw 3.09	oPw 2.28	oPw 4.69
oPw 3.04	tPw 3.40	Cu 1.70	Zn 3.00	Zn 1.90	As 4.33
Zn 3.00	As 2.00	As 1.67	As 2.33	tPw 1.85	tPw 4.07
Mg 2.95	Co 1.00	Co 1.20	tPw 1.98	Mg 1.70	Zn 3.86
tPw 2.65	Ni 1.00	Zn 1.15	Co 1.50	Pb 1.68	Cu 2.90
Co 1.40	Mg 0.98	Mg 0.98	Mg 1.28	Al 1.57	Mg 2.24
Mn 1.26	Zn 0.96	Pb 0.91	Al 1.14	K 1.55	Al 1.75
Al 1.25	P 0.93	Al 0.81	P 1.06	Co 1.50	Ti 1.60
Cu 1.10	Ti 0.82	Ti 0.81	K 1.06	Ti 1.33	Co 1.60
Ni 0.67	Cu 0.75	Ni 0.67	Ti 1.01	Ni 1.33	P 1.45
P 0.60	Mn 0.74	K 0.60	Ni 1.00	P 1.11	K 1.40
Ti 0.50	Al 0.73	Fe 0.60	Si 0.80	Fe 1.11	Ni 1.33
Fe 0.36	Fe 0.72	P 0.58	Cu 0.75	Si 0.99	Mn 1.19
Si 0.28	K 0.49	Mn 0.56	Ca 0.74	Sr 0.89	Fe 1.09
Cr 0.23	Si 0.30	Ca 0.37	Mn 0.65	Mn 0.87	Sr 1.07
Ca 0.22	Ca 0.25	Si 0.25	Sr 0.64	Cu 0.75	Si 0.87
K 0.21	Sr 0.17	Sr 0.20	Fe 0.58	Ca 0.63	Ca 0.79
Sr 0.19	Cr 0.15	Cr 0.11	Cr 0.07	Cr 0.27	Cr 0.48

Arsenic / Phosphorus

Arsenic is widely varying in both lakes at all depths. Phosphate varies less, although in lake Westeinder the inhomogeneity factor HI varies from 1.27-3.43. In lake Elfhoeven this factor is clearly smaller, especially in the toplayers of the sediment. In chapter VII, phosphate will be dealt with in detail.

Aluminum

The aluminum content in the sediments of the two lakes is varying indeed but only in the deeper layers of lake Westeinder this heterogeneity is considerably, with a factor of horizontal inhomogeneity exceeding the value 4. In the sediments in both lakes the factor HI is decreasing for aluminum with depth from 1 -10 cm and increasing again deeper into the sediment.

Silicon

The silicon content is quite constant in the sediments of the two lakes. This is logical because it represents the sand fraction of the sediment.

Magnesium / Calcium / Strontium

The variation of magnesium is larger in all cases than the variation of calcium. The same conclusion can be drawn with calcium in respect to strontium except for the deepest layer in lake Elfhoeven. The lighter element thus varies most in horizontal direction. This comparison with the order of the periodic table of the elements could not be made in respect to phosphorus towards arsenic.

The variation of magnesium, expressed by HI, shows the same overall view in both lakes: variation in the toplayer is high, in the sedimentlayers from 5-10 cm this variation is about average and increases again in the deeper layers. In both lake Westeinder and lake Elfhoeven the values of HI are amongst the upper 50 % in the order of magnitude

The inhomogeneity of calcium is average (Westeinder) to low (Elfhoeven) in the upper 10 cm of the sediments and increases in the deeper layers. In lake Elfhoeven this is even more with strontium; to a lesser degree this is also valid for lake Westeinder.

Potassium

The variation in potassium content in lake Elfhoeven sediments in increasing with depth. The same is observed in lake Westeinder.

Lead

Lead is one of the most strongly variable elements. At several cases it is the most varying one in both sediments. Deeper in the sediments, the variation of the lead content is less pronounced.

5.4 DETERMINATION OF MOST AND LEAST VARYING ELEMENTS

Comparison and interpretation of the data from tables 9, 10 and 11 is now followed by a classification. All data and conclusions so far are given for each of the five depths in the sediment separately. The classification method is explained for the classification of horizontal variability. It is also used for the vertical variability further on in this chapter.

Several methods to classify the elements on the basis of the calculated HI factors were compared and an easy scoring method was adopted: from the numerically sorted listings of HI (table 11), the occurrence of the 5 most varying elements per sediment layer was scored as well as the occurrence of the 5 least varying elements. The occurrences were expressed as a percentual occurrence.
A score of 100 % means occurrence at all 5 depths in the sediment and the element thus is very widely spreaded (5 occurrences in the listings of most varying elements) or very homogeneous element (5 occurrences in the listings of least varying elements). Other methods were also tried. Results differed on details from the used scoring method. These differences were small and the methods are thus not dealt with in detail. The results of the scoring method are listed in section discussion.

5.5 VERTICAL INHOMOGENEITY

In order to be able to compare the horizontal and vertical heterogeneity the vertical heterogeneity (symbol VI) was calculated the same way as the horizontal. VI thus is defined as the ratio range over average concentration per core for each one of the elements. The average concentration is calculated as mean on five depths in each core. The range is the maximum minus minimum and is also calculated for each core and each element.
Grouped per core and per element the values for VI are shown in the tables 12 and 13. The values of VI, arranged according to their size, thus result in the tables 14 and 15. From tables 14 and 15, listings of the most and least varying elements can be made the same way as was done with horizontal inhomogeinities. The same easy scoring method was used as in horizontal direction. Scoring results are shown in tables 16 and 17. A 100 % score means occurrence in all 17 cores in lake Westeinder or in all 13 cores in lake Elfhoeven (14 and 15) either as most or as least variable element (tables 16 and 17).

5.6 DISCUSSION ON THE OBSERVED VARIABILITY WITHIN THE SEDIMENTS

In tables 16 and 17, the variability in both directions is combined. This enables us to compare directly the horizontal and vertical inhomogeneity. Table 16 shows the most varying

Table 12.

Vertical inhomogeneity Westeinder, sequential per element

core element	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17
oPw	1.71	2.51	0.27	1.85	1.56	0.72	0.14	0.30	0.36	1.67	1.88	1.38	0.56	0.77	1.72	2.19	1.32
tPw	1.65	1.47	0.95	0.41	2.18	1.22	2.41	0.42	0.31	1.25	0.69	1.14	0.39	0.98	2.50	0.90	1.01
P	1.43	0.80	0.21	0.99	0.96	1.26	1.17	1.68	0.79	1.14	2.07	1.26	1.28	1.15	1.06	0.70	0.07
Al	2.95	1.54	0.46	0.77	1.57	1.52	0.89	0.78	1.91	2.67	1.65	1.20	0.93	2.05	1.53	0.20	0.68
As	1.65	3.00	1.50	2.18	2.92	2.14	1.25	1.78	2.50	1.54	2.50	1.86	2.22	2.78	1.82	1.36	1.79
Ca	0.29	2.29	1.54	0.30	0.60	0.91	0.19	0.80	1.45	0.62	1.18	0.61	1.16	1.32	1.14	0.23	1.01
Co	0.19	3.00	1.52	0.71	1.09	0.32	1.23	4.00	3.18	1.20	1.86	5.00	1.39	1.90	1.51	0.53	0.94
Cr	0.46	1.76	0.08	0.12	0.26	0.29	0.33	0.48	0.30	0.35	0.16	0.10	0.39	1.28	0.26	0.09	0.08
Cu	1.11	1.66	0.90	0.66	1.51	1.30	1.31	0.82	2.02	0.59	1.05	2.71	2.77	3.35	2.16	1.28	2.58
Fe	0.59	1.00	0.66	0.03	0.96	0.09	0.58	0.78	2.08	0.44	1.08	1.76	0.91	0.95	0.84	0.20	0.27
K	0.82	1.18	0.45	0.15	0.10	0.62	0.31	0.48	0.55	0.46	1.03	0.73	0.31	1.12	0.20	0.33	0.24
Mg	1.39	1.16	1.31	3.00	2.64	-	1.95	-	1.72	0.78	0.74	2.88	1.75	0.73	1.68	0.14	1.38
Mn	0.54	1.84	1.46	0.35	1.35	0.50	0.61	1.76	1.78	1.16	0.57	1.73	0.67	0.77	0.47	0.41	1.29
Ni	1.49	1.37	0.84	0.30	1.29	1.70	1.57	0.90	2.50	0.13	1.02	1.00	0.37	0.86	0.61	0.33	0.67
Pb	2.07	0.50	1.58	1.79	1.73	2.74	1.22	4.00	2.43	1.45	1.98	2 29	1.58	1.48	2.02	1.10	2.11
Si	0.37	0.89	0.11	0.27	0.40	0.59	0.41	0.58	0.69	0.41	0.54	0.76	0.73	0.62	0.11	0.11	0.57
Sr	0.16	1.24	0.85	0.12	0.10	0.14	0.18	0.38	0.45	0.40	0.42	0.51	0.48	0.39	0.61	0.17	0.24
Ti	1.97	1.41	0.64	0.47	1.25	1.10	1.15	1.08	1.81	1.71	1.52	3.17	1.64	1.53	0.95	0.50	0.82
Zn	0.98	0.11	0.17	1.08	1.11	1.17	1.36	4.00	1.71	1.37	1.35	0.22	1.01	1.48	1.09	1.20	1.36

elements, table 17 shows the least varying elements in the lakebeds of both lakes.

Now, the variation is compared in horizontal and vertical direction and for the two lake sediments. Subsequently:
(1) horizontal inhomogeneity in lake Westeinder towards that in lake Elfhoeven
(2) vertical inhomogeneity in lake Westeinder towards that in lake Elfhoeven
(3) horizontal towards vertical inhomogeneity in both lakes
(4) the inhomogeneity of lake Westeinder sediments towards that in lake Elfhoeven sediments in both directions

The following classification method for determination of the degree of variability is adopted: an element mentioned in table 16 or 17 is called
<u>strongly inhomogeneous</u> when the relative occurrence exceeds or equals 40 % which means occurrence in at least 2 of the 5 sediment depth layers or in at least 7 of 17 cores (Westeinder) resp. in at least 6 of 13 cores (Elfhoeven)
<u>moderately inhomogeneous</u> when the relative occurrence of this element exceeds or equals 40 % in one of the two directions and is less than 40 % in the other direction
<u>homogeneous</u> when the relative occurrenc is less than 40 % in both directions.

From this, table 18 summarizes the degree of horizontal and vertical inhomogeneity in both lake Westeinder and lake Elfhoeven sediments. It is subdevided in nine sections:

Table 13.

Vertical inhomogeneity Elfhoeven, sequential per element

core element	18	19	20	21	22	23	24	25	26	27	28	29	30
oPw	1.76	1.33	3.75	1.50	1.66	1.83	2.24	2.85	1.49	0.47	0.62	0.70	1.68
tPw	2.78	1.16	1.91	0.37	1.61	1.25	1.13	0.89	2.20	0.55	1.00	0.73	1.40
P	0.60	0.63	0.67	0.55	1.03	0.28	0.16	0.46	0.48	0.51	0.64	0.20	0.52
Al	0.24	0.42	0.79	0.83	2.01	1.25	0.61	0.65	0.89	0.30	0.33	0.07	0.34
As	0.75	2.19	5.00	0.88	2.00	1.67	0.01	2.06	1.50	2.00	2.14	1.80	3.44
Ca	0.16	0.06	0.59	0.32	0.14	0.44	0.70	0.31	0.10	0.31	0.40	0.10	0.11
Co	0.19	0.24	1.04	0.40	2.40	1.45	0.48	0.21	0.35	0.51	0.40	0.14	0.13
Cr	0.12	0.15	0.37	0.26	0.35	0.12	0.07	0.11	0.07	0.18	0.11	0.00	0.22
Cu	0.00	1.00	1.44	0.94	1.67	0.84	0.56	1.33	0.65	1.32	1.27	0.16	1.05
Fe	0.09	0.04	0.61	0.24	1.09	0.46	0.23	0.09	0.04	0.20	0.14	0.00	0.05
K	0.16	0.36	0.11	0.35	1.44	0.37	0.49	0.20	0.30	0.36	0.31	0.04	0.30
Mg	0.18	0.70	1.46	1.54	1.43	1.56	0.66	0.37	1.35	1.04	0.63	0.12	0.13
Mn	0.28	0.37	0.52	0.47	0.73	0.67	0.71	0.64	0.54	0.41	0.37	0.07	0.21
Ni	0.00	0.06	0.72	0.38	1.73	0.44	0.17	0.38	0.31	0.41	0.25	0.03	0.06
Pb	1.14	2.09	2.58	1.35	1.23	0.63	1.89	0.78	0.67	1.53	1.58	0.58	1.63
Si	0.13	0.16	0.33	0.61	0.95	0.31	0.28	0.25	0.04	0.30	0.28	0.06	0.03
Sr	0.19	0.62	0.14	0.33	0.52	0.13	0.24	0.09	0.10	0.18	0.13	0.08	0.08
Ti	0.25	0.31	0.78	0.34	1.38	1.03	0.59	0.55	0.35	0.29	0.48	0.03	0.32
Zn	0.17	1.35	0.39	1.62	1.89	1.29	1.98	1.14	1.20	1.80	0.94	0.04	1.37

(1) comparison of horizontal and vertical inhomogeneity in both lake Westeinder and lake Elfhoeven
(2) comparison of horizontal inhomogeneity in both lake Westeinder and lake Elfhoeven
(3) comparison of vertical inhomogeneity in both lake Westeinder and lake Elfhoeven
(4) comparison of horizontal and vertical inhomogeneity in lake Westeinder
(5) comparison of horizontal and vertical inhomogeneity in lake Elfhoeven
(6) degree of horizontal inhomogeneity in lake Westeinder
(7) degree of horizontal inhomogeneity in lake Elfhoeven
(8) degree of vertical inhomogeneity in lake Westeinder
(9) degree of vertical inhomogeneity in lake Elfhoeven

Some remarks are made on this table

Pb, As, oPw are strongly variable at all depths both in horizontal and vertical direction in both lake sediments.

P, Ni are moderately variable in horizontal and in vertical direction in Westeinder and Elfhoeven sediments.

Sr, Cr, Si are quite constant in both directions in both sediments. Silicon represents the obviously quite constant sand fraction in the bottom sediments.

Table 14.

Vertical inhomogeneity Westeinder, sequential per core

core	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17
	Al 2.95	As 3.00	Pb 1.59	Mg 3.00	As 2.92	Pb 2.74	tPw 2.41	Co 4.00	Co 3.18	Al 2.67	As 2.50	Co 5.00	Cu 2.77	Cu 3.35	tPw 2.50	oPw 2.19	Cu 2.58
	Pb 2.07	Co 3.00	Ca 1.54	As 2.18	Mg 2.64	As 2.16	Mg 1.95	Pb 4.00	As 2.50	Ti 1.74	P 2.07	Ti 3.17	As 2.22	As 2.78	Cu 2.16	As 1.36	Pb 2.11
	Ti 1.97	oPw 2.51	Co 1.52	oPw 1.85	tPw 2.18	Ni 1.70	Ni 1.57	Zn 4.00	Ni 2.50	oPw 1.67	Pb 1.98	Mg 2.88	Mg 1.75	Al 2.05	Pb 2.02	Mg 1.35	As 1.79
	oPw 1.75	Ca 2.29	As 1.50	Pb 1.79	Pb 1.73	Al 1.53	Zn 1.36	As 1.78	Pb 2.43	As 1.56	oPw 1.88	Cu 2.71	Ti 1.66	Co 1.90	As 1.82	Cu 1.28	Mg 1.38
	tPw 1.65	Mn 1.84	Mn 1.48	Zn 1.08	Al 1.57	Cu 1.30	Cu 1.31	Mn 1.76	Fe 2.08	Pb 1.45	Co 1.86	Pb 2.29	Pb 1.58	Ti 1.53	oPw 1.72	Zn 1.20	Zn 1.36
	As 1.65	Cu 1.66	Mg 1.31	P 0.99	oPw 1.56	P 1.26	As 1.25	P 1.68	Cu 2.02	Zn 1.37	Al 1.65	As 1.86	Co 1.39	Pb 1.68	Mg 1.68	Pb 1.10	oPw 1.32
	Ni 1.49	Al 1.54	tPw 0.95	Al 0.77	Cu 1.51	tPw 1.22	Co 1.23	Ti 1.08	Al 1.91	tPw 1.25	Ti 1.52	Fe 1.76	P 1.28	Zn 1.48	Al 1.53	tPw 0.90	Mg 1.29
	P 1.43	tPw 1.47	Cu 0.90	Co 0.71	Mn 1.35	Zn 1.17	Pb 1.22	Ni 0.93	Ti 1.81	Co 1.20	Zn 1.35	Mn 1.73	Ca 1.16	Ca 1.32	Co 1.31	P 0.70	Ca 1.01
	Mg 1.39	Ti 1.41	Sr 0.85	Cu 0.66	Ni 1.29	Ti 1.10	P 1.17	Cu 0.82	Mn 1.78	Mn 1.16	Ca 1.18	oPw 1.38	Zn 1.01	P 1.15	Ca 1.14	Co 0.53	tPw 1.01
	Cu 1.11	Ni 1.37	Ni 0.84	Ti 0.47	Ti 1.25	Ca 0.91	Ti 1.15	Ca 0.80	Mg 1.72	P 1.14	Fe 1.08	P 1.26	Al 0.93	K 1.12	Zn 1.09	Ti 0.50	Co 0.94
	Zn 0.98	Sr 1.24	Fe 0.66	tPw 0.41	Zn 1.11	oPw 0.72	Al 0.89	Al 0.78	Zn 1.71	Mg 0.78	Cu 1.05	Al 1.20	Fe 0.91	tPw 0.98	P 1.06	Mn 0.41	Ti 0.93
	K 0.89	K 1.18	Ti 0.64	Mn 0.35	Co 1.09	K 0.62	Mn 0.61	Fe 0.78	Ca 1.45	Ca 0.62	K 1.03	tPw 1.14	Si 0.73	Fe 0.95	Ti 0.95	K 0.33	Al 0.68
	Fe 0.59	Mg 1.16	Al 0.46	Ca 0.30	Fe 0.96	Si 0.59	Fe 0.58	Si 0.58	P 0.79	Cu 0.59	Ni 1.02	Ni 1.00	Mn 0.67	Ni 0.86	Fe 0.84	Ni 0.33	Ni 0.67
	Mn 0.54	Fe 1.00	K 0.45	Ni 0.30	P 0.96	Mn 0.50	Si 0.41	Cr 0.48	Si 0.69	K 0.46	Mg 0.74	Si 0.76	oPw 0.56	oPw 0.77	Ni 0.61	Ca 0.23	Si 0.57
	Cr 0.40	Si 0.89	oPw 0.27	Si 0.27	Ca 0.60	Co 0.32	Cr 0.33	K 0.48	K 0.55	Fe 0.44	tPw 0.69	K 0.73	Sr 0.48	Mn 0.77	Sr 0.61	Al 0.20	Fe 0.27
	Si 0.37	P 0.80	P 0.21	K 0.15	Si 0.60	Cr 0.29	K 0.31	tPw 0.42	Sr 0.45	Si 0.41	Mn 0.57	Ca 0.61	tPw 0.39	Mg 0.73	Mn 0.47	Fe 0.20	K 0.24
	Ca 0.29	Pb 0.50	Zn 0.17	Cr 0.12	Cr 0.26	Sr 0.14	Ca 0.19	Sr 0.38	oPw 0.36	Sr 0.40	Si 0.54	Sr 0.51	Cr 0.39	Si 0.62	Cr 0.28	Sr 0.17	Sr 0.24
	Co 0.19	Cr 0.33	Si 0.11	Sr 0.12	K 0.10	Fe 0.09	Sr 0.18	oPw 0.30	tPw 0.31	Cr 0.35	Sr 0.52	Zn 0.22	Ni 0.37	Sr 0.39	K 0.20	Si 0.11	Cr 0.09
	Sr 0.16	Zn 0.11	Cr 0.08	Fe 0.03	Sr 0.10	Mg 0.0	oPw 0.14	Mg 0.0	Cr 0.30	Ni 0.13	Cr 0.16	Cr 0.10	K 0.31	Cr 0.04	Si 0.11	Cr 0.09	P 0.07

Table 15.

Vertical inhomogeneity Elfhoeven, sequential per core

core	18	19	20	21	22	23	24	25	26	27	28	29	30
	tPw 2.78	As 2.19	As 5.00	Zn 1.62	Co 2.40	oPw 1.83	oPw 2.24	oPw 2.85	tPw 2.20	As 2.00	As 2.14	As 1.80	As 3.44
	oPw 1.76	Pb 2.09	oPw 3.75	Mg 1.54	Al 2.01	As 1.67	As 2.20	As 2.06	As 1.50	Zn 1.80	Pb 1.58	tPw 0.73	oPw 1.68
	Pb 1.14	Zn 1.35	Pb 2.58	oPw 1.50	As 2.00	Mg 1.56	Zn 1.98	Cu 1.33	oPw 1.49	Pb 1.53	Cu 1.27	oPw 0.70	pb 1.63
	As 0.75	oPw 1.33	tPw 1.91	Pb 1.35	Zn 1.89	Co 1.45	Pb 1.89	Zn 1.14	Mg 1.35	Cu 1.32	tPw 1.00	Pb 0.58	tPw 1.40
	P 0.60	tPw 1.16	Mg 1.46	Cu 0.94	Ni 1.73	Zn 1.29	tPw 1.13	tPw 0.89	Zn 1.20	Mg 1.04	Zn 0.94	P 0.20	Zn 1.37
	Mn 0.28	Cu 1.00	Cu 1.44	As 0.88	Cu 1.67	Al 1.25	Mn 0.71	Pb 0.78	Al 0.89	tPw 0.55	P 0.64	Cu 0.16	Cu 1.05
	Ti 0.25	Mg 0.70	Co 1.04	Al 0.83	oPw 1.66	tPw 1.25	Ca 0.70	Al 0.65	Cu 0.67	P 0.51	Mg 0.63	Co 0.14	P 0.52
	Al 0.24	P 0.63	Al 0.79	Si 0.61	tPw 1.61	Ti 1.03	Mg 0.66	Mn 0.64	Pb 0.65	Co 0.51	oPw 0.62	Mg 0.12	Al 0.34
	Co 0.19	Sr 0.62	Ti 0.78	P 0.55	K 1.44	Cu 0.84	Al 0.61	Ti 0.55	Mn 0.54	oPw 0.47	Ti 0.48	Ca 0.10	Ti 0.32
	Sr 0.19	Al 0.42	Ni 0.72	Mn 0.47	Mg 1.43	Mn 0.67	Ti 0.59	P 0.46	P 0.48	Mn 0.41	Co 0.40	Sr 0.08	K 0.30
	Mg 0.18	Mn 0.37	P 0.67	Co 0.40	Ti 1.38	Pb 0.63	Cu 0.56	Ni 0.38	Co 0.35	Ni 0.41	Ca 0.40	Al 0.07	Cr 0.22
	Zn 0.17	K 0.36	Fe 0.61	Ni 0.38	Pb 1.23	Fe 0.46	K 0.49	Mg 0.37	Ti 0.35	K 0.36	Mn 0.37	Mn 0.07	Mn 0.21
	Ca 0.16	Ti 0.31	Ca 0.59	tPw 0.37	Fe 1.09	Ca 0.44	Co 0.48	Ca 0.31	Ni 0.31	Ca 0.31	Al 0.33	Si 0.06	Mg 0.13
	K 0.16	Co 0.24	Mn 0.52	K 0.35	P 1.03	Ni 0.44	Si 0.28	Si 0.25	K 0.30	Al 0.30	K 0.31	K 0.04	Co 0.13
	Si 0.13	Si 0.16	Zn 0.39	Ti 0.34	Si 0.95	K 0.37	Sr 0.24	Co 0.21	Ca 0.10	Si 0.30	Si 0.28	Zn 0.04	Ca 0.11
	Cr 0.12	Cr 0.15	Cr 0.37	Sr 0.33	Mn 0.73	Si 0.31	Fe 0.23	K 0.20	Sr 0.10	Ti 0.29	Ni 0.25	Ni 0.03	Sr 0.08
	Fe 0.09	Ca 0.06	Si 0.33	Ca 0.32	Sr 0.52	P 0.28	Ni 0.17	Cr 0.11	Cr 0.07	Fe 0.20	Fe 0.14	Ti 0.03	Ni 0.06
	Cu -	Ni 0.06	Sr 0.14	Cr 0.26	Cr 0.35	Sr 0.13	P 0.16	Fe 0.09	Fe 0.04	Cr 0.18	Sr 0.13	Cr -	Fe 0.05
	Ni -	Fe 0.04	K 0.11	Fe 0.24	Ca 0.14	Cr 0.12	Cr 0.07	Sr 0.09	Si 0.04	Sr 0.18	Cr 0.11	Fe -	Si 0.03

tPw, Zn The total phosphate content in the interstitial water and the zinc content are strongly varying in both lake Westeinder and lake Elfhoeven sediments in horizontal direction. In lake Westeinder in vertical direction the variation is moderate. In lake Elfhoeven total-phosphate and zinc are strongly varying in vertical direction again.

Co Cobalt is moderately spreaded in both lakesediments in horizontal direction and in lake Elfhoeven also in vertical direction. It is strongly spreaded in lake Westeinder sediments in vertical direction.

Table 16.

Most varying elements in the sediments of both lakes

Percentual occurrence of most varying elements of both lake sediments in both horizontal and vertical direction.
A 100 % score means occurrence in all layers (horizontal) *and/or in all cores (vertical) of lake* Westeinder and in lake Elfhoeven sediments resp.

Most varying elements in lake Westeinder sediments

Horizontal	score	Vertical	score
tPw	80	As	82.4
		Pb	76.5
Mg, Pb, oPw,		Cu	47.1
Ti, Zn, As	60	oPw, Mg, Co	41.1
Al	40	Ti, Al, Zn	29.4
Co	20	tPw	23.5
		Ni, Mn	17.6
		Ca	11.8
		P, Fe	5.9

Most varying elements in lake Elfhoeven sediments

Horizontal	score	Vertical	score
As, oPw	100	As	92.3
tPw	80	oPw, Zn	76.9
Pb, Zn	60	Pb, tPw	69.2
Co, Mg	40	Mg	38.5
Cu	20	Cu	30.8
		Co, P	15.4
		Ni, Al	7.7

Ti, Al Titanium and Aluminum are moderately varying in vertical direction in both lake sediments. This is also the case in vertical direction in lake Westeinder. In horizontal direction in lake Westeinder these elements are quite varying.

Fe The iron contents are moderately spreaded in both lake sediments in the horizontal direction. In vertical direction the iron-contents vary moderately in lake Westeinder and are quite constant in lake Elfhoeven sediments.

K The heterogeneity of potassium in the sediments of lake Westeinder is small in both horizontal and vertical direction. In lake Elfhoeven both vertical and horizontal heterogeneity is moderately.

Ca Calcium is moderately inhomogeneous spread in vertical direction in lake Elfhoeven sediments and uniformly distributed in horizontal direction in both lake sediments and in vertical direction in lake Westeinder sediments.

Cu Copper appears to be moderately variable in the sediments in both directions in lake Elfhoeven. In lake Westeinder copper is strongly inhomogeneous in vertical direction and moderately in horizontal direction. This will be further elucidated in chapter VI.

Mn Manganese contents are moderately variable in vertical direction in both lakesediments and in vertical direction in the bottom of lake Elfhoeven. The manganese variation is small in horizontal direction in both lake Elfhoeven and Westeinder sediments.

Table 17.

Least varying elements in the sediments of both lakes

Percentual occurrence of the least varying elements of both lake sediments in both horizontal and vertical direction.
A 100 % score means occurrence in all layers (horizontal) *and/or in all cores (vertical) of lake* Westeinder and in lake Elfhoeven sediments resp.

Least varying elements in lake Westeinder sediments

Horizontal	score	Vertical	score
Cr, Sr,	100	Cr	94.1
Si, K, Ca	*60*	*Sr*	*88.2*
Mn, Cu	40	Si	58.8
Fe, P	20	K	52.9
		Fe	29.4
		Ca, oPw, tPw	23.5
		Mg, Zn, P	17.6
		Ni, Co	11.8
		Pb, Al	5.9

Least varying elements in lake Elfhoeven sediments

Horizontal	score	Vertical	score
Cr, Sr, Ca	100	Cr	92.3
Si, Mn	60	Sr, Fe	76.9
K	40	Si	69.2
Fe, Cu	20	Ni	46.2
		Ca	38.5
		K, Ti	23.1
		P, Zn	15.4
		Mn, Cu, Co	7.7

Table 18.

Distribution in the two lakes and in both directions

Variation note 1) S	M	L	Direction note 2) Hor	Ver	Lake note 3) WE	Elf	Elements that satisfy the criteria
+			+	+	+	+	As, Pb, oPw
	+		+	+	+	+	P
		+	+	+	+	+	Cr, Si, Sr
+			+		+	+	As, Mg, Pb, Zn, oPw, tPw
	+		+		+	+	Fe, Ni, P
		+	+		+	+	Cr, K, Mn, Si, Sr
+				+	+	+	As, Pb, oPw
	+			+	+	+	Al, Ca, Mn, P, Ti
		+		+	+	+	Cr, Si, Sr
+			+	+	+		As, Mg, Pb, oPw
	+		+	+	+		Fe, Ni, P
		+	+	+	+		Cr, K, Si, Sr
+			+	+		+	As, Pb, Zn, oPw, tPw
	+		+	+		+	Al, Cu, Mg, P, Ti
		+	+	+		+	Cr, Si, Sr
+			+		+		Al, As, Mg, Pb, Ti, Zn, oPw, tPw
	+		+		+		Co, Fe, Ni, P
		+	+		+		Ca, Cr, Cu, K, Mn, Si, Sr
+			+			+	As, Co, Mg, Pb, Zn, oPw, tPw
	+		+			+	Al, Cu, Fe, Ni, P, Ti
		+	+			+	Ca, Cr, Mn, Si, Sr
+				+	+		As, Co, Cu, Mg, Pb, oPw
	+			+	+		Al, Ca, Fe, Mn, Ni, P, Zn, tPw
		+		+	+		Cr, K, Si, Sr
+				+		+	As, Pb, Zn, oPw, tPw
	+			+		+	Al, Ca, Co, Cu, K, Mg, Mn, P, Ti
		+		+		+	Cr, Fe, Ni, Si, Sr

1) S = Strongly variable, M = Moderately variable and
L = Low variability as defined before in the text
2) Hor = Horizontal and Ver = Vertical direction
3) *WE = Lake Westeinder, Elf = Lake Elfhoeven*

Chapter VI

DISTRIBUTION PATTERNS OF COPPER IN THE SEDIMENTS

6.1 INTRODUCTION

From chapter X it appears, that the copper-concentrations in the toplayer of the sediments in the two lakes are much higher than in all deeper layers of the sediments. Indeed, copper is one of the elements where statistical noise is sufficiently low to discern patterns in the distribution. In lake Westeinder the concentrations are 1.5-2 times higher than in lake Elfhoeven. A sharp decrease just below the toplayer was observed in nearly all cores in both lakes (fig. 12). In this chapter, the distribution of copper in the sediments is discussed with emphasis on the high amount of copper in the toplayers.

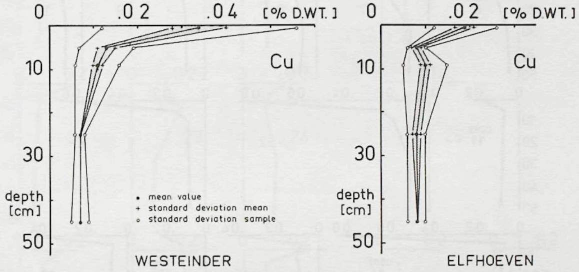


Figure 12: Average copper profiles in Westeinder and Elfhoeven sediments

It also appeared, that strong copper accumulations occurred in the south-western part of lake Westeinder in the toplayers. This indicates a recent copper input, resulting in the observed sharp vertical profiles. The penetration depth of copper in lake Westeinder sediments is larger than in lake Elfhoeven sediments. The copper-concentrations in deeper layers are about the same in both lakes. This can mean that the copper inputs in the past for the two lakebeds were similar. The standard deviations, as shown in table indicate, that the observed structures are reliable. They are detailed in the next sections.

6.2 HORIZONTAL PATTERN IN THE DISTRIBUTION OF COPPER

In the south-western part of lake Westeinder, a group of cores showed copper contents in the toplayer, that were considerably higher than the concentrations in the rest of the lake. The cores were considered to show high concentrations when the copper-content in the toplayer was higher than the algebraic sum of samplemean and standard deviation, being 0.040 % Cu. This is shown in figures 13 and 14.

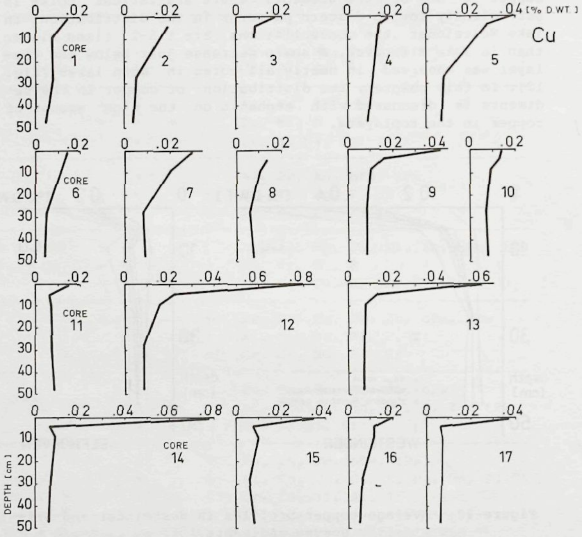


Figure 13: Copper depth profiles in lake Westeinder sediments

In lake Elfhoeven little horizontal structure was observed (figure 15). The highest concentrations in lake Westeinder *sediments were found in the toplayers of the sediments on* the sampling locations 2, 7, 8, 9, 12, 13, 14 and 17. This area with high concentrations in the toplayers is the region where the water from the Ringvaart canal enters the lake. This strongly indicates the Ringvaart as source of copper. As a consequence the binding processes must be fast as compared to horizontal mixing of the lakewater. From low and

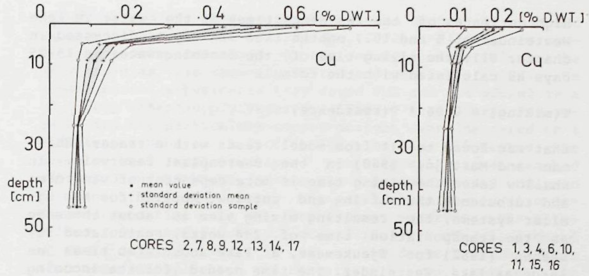


Figure 14: Geographically different depth profiles in lake Westeinder

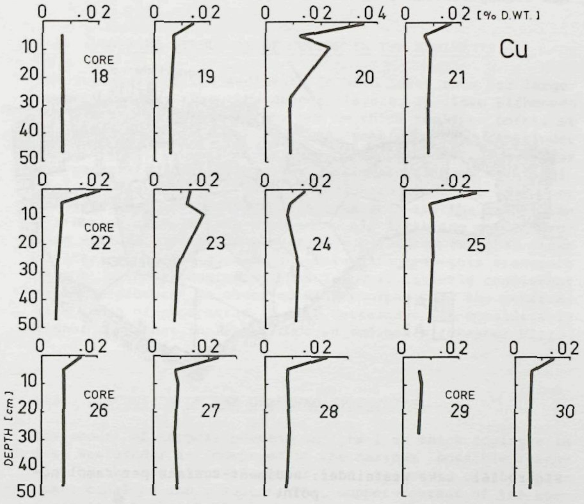


Figure 15: Copper depth profiles in lake Elfhoeven sediments

high estimates of the residence times of the water in lake Westeinder of 5 and 10.7 months (150-325 days), discussed in chapter VII, the mixing time of the incoming water is 15-25 days as calculated with the formula

T(mixing) = 0.06 * T(residence)

that was found to fit from model tests with a tracer (Huisman and Martijn, 1968) in the Beerenplaat reservoir. In shallow lakes the mixing time is more dependent of windforce and turbulence than of in- and outflow. Applied for two similar systems, the resulting mixing time is about the same as the transportation time of 2-4 weeks, calculated by Leenen (1982) for Tjeukemeer, a lake about two times as large as lake Westeinder. The time needed for the incoming water to flow from the inlet across lake Westeinder and spread over the area with high copper-contents -surface A(1) in figure 16- is now approximated by the ratio of the surfaces A(1) and A(1)+A(2). A(2) represents the other part of the lake. This ratio is about 0.6, thus resulting in a maximum transportation time of the copper of 5-12 days.

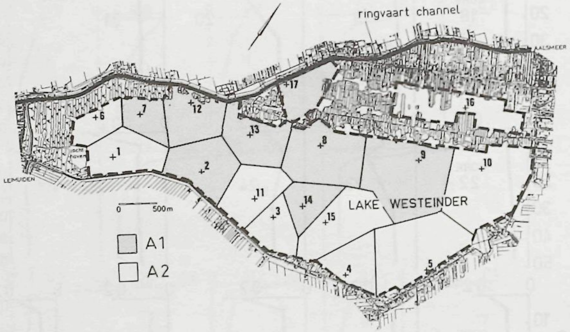


Figure 16: Lake Westeinder: sediment-surface per sampling-point

If a significant part of the excess copper in the sediments originates from the lake water, the calculated mixing time of the water and the time of copper removal from the water are probably about the same. Some data on the binding of copper by particles, algae and sediments are given below. Copper is well-known to concentrate in organic-rich sediments. The incorporation mechanism is probably initiated by the formation of chelate complexes when copper is adsorbed on particulate matter (Fairbridge, 1972). Binding or complexation onto compounds in the sediment material can be very rapid as was shown by Button and Hostetter (1977). In algal control experiments they dosed 0.2 and 0.4 gCu/m2 in a 18 m deep water-supply reservoir (Hoover reservoir). The soluble and the particulate copper-content were measured on 4 different depths as a function of time. At all depths, the soluble Cu(2+)-values dropped to original values reached after 2.5 and 24 hours in the two experiments resp. only in the case of 0.2 gCu dosage. The particulate copper also decreased with time. In the Beerenplaat reservoir, the Netherlands, dosages of 0.05-0.1 gCu/m3 (0.3-0.6 gCu/m2) dropped to their original levels in one or two days. This is longer than measured by Button and Hostetter, but much smaller than the mixing time for the water in the Beerenplaat reservoir of about two weeks It is noted, that the Beerenplaat reservoir is divided is seven separate reservoirs by small dams to diminish the short-circuiting and thus decrease the mixing in the reservoir.

6.3 VERTICAL STRUCTURE OF COPPER IN THE SEDIMENTS

The toplayers of the sediments in both lakes show far larger copper-contents than the deeper layers. In lake Elfhoeven the additional copper in the one cm thick toplayer points at a recent input increase of 0.33 tons. In lake Westeinder this toplayer contains 6.7 tons of copper. Moreover copper has penetrated deeper into the sediments (figure 12), indicating other inputs or vertical downward transport of copper in Westeinder sediments. Possible causes are the higher infiltration rate in lake Westeinder and filtering and adsorption effects in the toplayer of the sediments that cause 'filtering' of the copper. In lake Elfhoeven this transport is not clearly observed. This is qualitatively consistent with the picture we observed with phosphorus: the penetration depth of phosphorus in lake Westeinder was considerably higher than that in lake Elfhoeven sediments (Chapter VII).

6.4 DISCUSSION ON THE OBSERVED STRUCTURES

The amount of copper, present in the 1 cm thick toplayer in lake Westeinder is compared to the maximum possible retention by the sediments of copper from the water of the Ringvaart canal as input source. The copper-content of the toplayer is calculated from the sediment watercontent and the copper concentration in the upper toplayer of 1 cm thickness on those sampling locations where the high content was measured. The calculation, using weighed sediment-surfaces for each sampling point (2, 7, 8, 9, 12, 13, 14 and 17), results in an amount of copper of 6.72 tons in the 1 cm thick toplayer (table 19).
The schematization is given in figure 16. The total copper-content of the inflowing water is 10 ppb Cu. This value is calculated as average for the period of august and november

Table 19.

Copper-contents in Westeinder sediments: 0-1 cm depth

sampling subarea	copper content	water content	copper amount per subarea
	% of dry weight	% of weight	tons Cu
2	0.040	98.3	0.10
7	0.030	73.6	0.57
8	0.045	97.9	0.16
9	0.042	95.4	0.55
12	0.080	55.5	4.38
13	0.059	95.9	0.36
14	0.077	95.5	0.31
17	0.040	90.3	0.29
Total amount of copper in area A(1)			6.72

1981 the period of the field work of this study of the concentrations on three existing water quality sampling points of the waterboard in the direct surroundings of the lake; two points in the Ringvaart canal (26A and 57) and one point (161.01) in the polderwater near Leimuiden (Rijnland, yearreport). Using a flow rate in the Ringvaart canal of 2 m3/s the input and so the maximum retention is 0.6 tons of copper per year and corresponds with an input during at least 10 years (table 19). The consistency of the results in a large number of samples taken indicate, that the data give a representative view of that particular lakearea. The assumption that all supplied copper is retained by the sediment, as upper limit is unrealistic but if the retention is smaller, the ratio between actual deposition and input even becomes larger than 10 and the time of input becomes larger than 10 years.

The above mentioned possibility of long time input is not the only reason for the existence of accumulations. The high copper-contents in the toplayer and the sharp decrease with depth are likely to be the result of a superposition of several processes. The yearly copper input, being 10 % of the total amout of copper in the 1 cm thick toplayer of the sedimentarea, covering 50 % of the lakearea, suggests timescales of the processes of flattening of the accumulations due to the dispersion processes bioturbation and windturbation of several years. If high contents of an element occur in the utmost toplayer of the sediments, as is the case for copper and phosphorus, than the peak-flattening mixing effects of windturbation and bioturbation must be small. This can also be illustrated as follows. When the toplayer of the sediment with a thickness of 2 mm, a watercontent 90 % and a density of 2500 kg/m3 is brought in suspension in the 2.5 m deep lake Westeinder, this results in a for surface-water

very high suspended solids concentration of 200 g/m3. This corresponds with de Gruyter and Molt (1957). Studies on the amount and chemistry of resuspended material and its local variation can be of great importance. We know actually very little about sedimentation and transport in these systems. Questions like: is resuspension linear with windforce and do processes like resettlement cause pattern formation are directly open for research. The latter question can for instance be done with simulated fractionation in centrifuges. Observations in the field must be made in advance.

Reasons for the large difference between maximum possible input and observed concentrations in the sediments can be:
(1) transport of sediment material from the Ringvaart canal to the lake
(2) differences in infiltration rates in the lakes as compared to wind
(3) differences due to a better mixing of the water in lakearea A(1) (figure 16) by which inputs are bound predominantly in the particular area
These points are detailed below

ad (1)
Removal of copper from the surface-water by amongst others sedimentation may have caused the high contents. Again, this is consistent with the pattern we observed with phosphorus, the number of data available is far less however. In lake Westeinder, the vertical copper profiles are characterized by extra transportmechanisms. The high observed copper-contents in area A(1) can also partly be caused by another horizontal transportmechanism of copper. Next to transport with particles in the surface water, an additional coppersupply can be provided by material transported rolling on the bottom, or settling material when water enters the lake and the water velocity decreases. This material enters the lake in the south-western part and is likely to settle in the lake more permanently than in the Ringvaart canal. This mechanism can contribute to the measured accumulation.

ad (2)
A reason that is possibly contributing to the large amounts of copper in the toplayers of the sediments in the south western part of lake Westeinder is the difference in infiltration rate within the lake. The groundwater table in the centre of the lake is higher than at the shores, as is illustrated with the geo-hydrological profile, suggesting a higher infiltration rate at the shores (fig. 17).
Next to this, the groundwaterlevel under polder Haarlemmermeer is lower than the level under the polders at the eastside of the lake (Rijnland, Technical Services). The permeability of the aquifer underneath the lake and the values of flow resistance of the covering layer do not differ much (Wit, 1974) and thus will not contribute.
These differences in infiltration rates in lake Westeinder will probably contribute to differences in the shapes of the profiles. The rate is about 1 mm/day and therefore it can not be the only cause for the transport of copper and phosphate from the water to the sediments. The reverse, sediment as indicator for upwelling, is discussed by Dieter-Haass (1978).

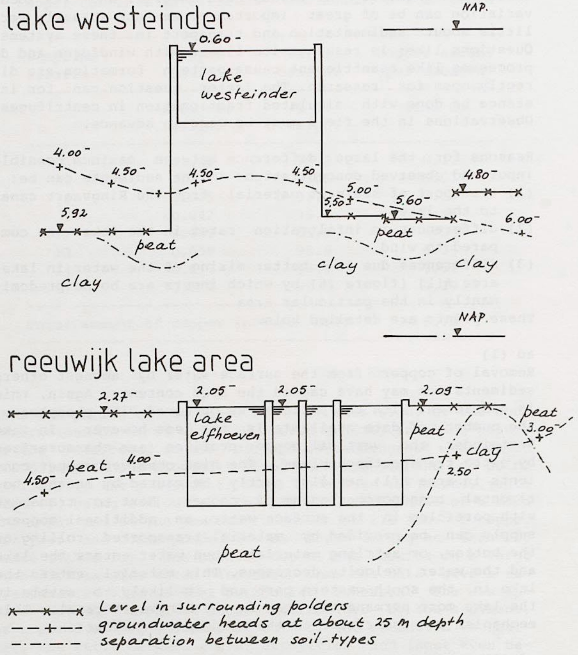


Figure 17: Geo-hydrological profile on both lakes

ad (3)
The copper can also be removed from the incoming water by chemical sorption processes on sediments and sedimenting material, before the water reaches the other shore of the lake. This occurs when the chemistry of inflowing water and lakewater is different and results in the observed local accumulations in the toplayer, schematically represented by figure 16. A(1) represents the surface part of the lake with high toplayer copper contents, A(2) represents the other part of the lake. Two sources of copper that are part

of the input from the Ringvaart canal, is dung of pigs in stock-farms and the application of copper as tubes in drinking water supply. Copper as tube-material replaced lead during the last decades. The observed lower lead contents in the toplayers of both lake sediments can be consistent with this. With the available data, more detailed conclusions on this are not possible, the subject however is open to further research.

If mechanisms of bottom particle transport from the Ringvaart canal to the lake, followed by vertical transport due to higher vertical transport rates occur in the south western part of lake Westeinder, than the depth profiles must reflect this by higher contents to larger depths. This is indeed observed for copper in the cores: 7, 8, 9, 12 and 15.
The average phosphorus profiles do show the same picture to a depth of about 30 cm (next chapter), but now at all sampling locations in the toplayer.

In lake Westeinder the high concentration in the toplayer shows both a horizontal and a vertical structure within the lake.

In lake Elfhoeven sediments, only a vertical structure was observed. Some reasons are:

(1) less transport of particles from the Breevaart. The inflow of water in lake Westeinder differs from that in the Reeuwijk lake area. The waterdepth at the connection between the Breevaart and lake Elfhoeven is about 1.5 m. The waterdepth in the fairway in the Breevaart as well as in lake Elfhoeven itself are larger. The connection thus forms a kind of underwater-bar, allowing only a limited transport of bottommaterial. It may very well be that the difference in entering possibilities of the bottom material in the Ringvaart canal and in the Breevaart contributed to the observed differences in composition of the sediments in both lakes.
(2) reasons of scale: lake Elfhoeven is smaller than the area in lake Westeinder, where the high copper-contents were observed. The time required for mixing will probably be smaller in lake Elfhoeven, resulting in a relative better mixed waterbody and a more even spreaded copper-content of the sediment. The influence of the smaller flow in lake Elfhoeven is not included in this discussion, however. If the flow, entering lake Elfhoeven is smaller, than the time required for mixing increases again. The differences in sorption capacity of the sediments of lake Westeinder and lake Elfhoeven can in that case have contributed to the observed differences.

When the influences of windturbation and bioturbation is small, this has its consequences on sediment modelling. Terms for windturbation and bioturbation must be introduced now as locally different within one lake. A model with one uniform value for these types of processes will perforce result in wrong conclusions when applied on scales smaller than the dimensions of the lake. This must especially be avoided when the exchange processes across the sediment-water interface are terms in the model. Existing differences in the characteristics of the sediment should be included in the development of these models, as much as possible.

In this respect de Groot (1981) found a negative correlation between phosphate desorption flux and the wind (a rising wind tends phosphate levels to drop). This was also observed by Conally et al (1983). In some cases, suspension of sediments was shown to transport a significant mass of pollutant to new sorption sites. Logical questions from this are:
(1) if a storm event occurs with, for instance, windforce 10 during 24 hours, how many sediment is resuspended, order 1 mm or 10 cm. If the resuspended layer is thick, than a mixing of the toplayer must be followed by a rapid re-buildup of the copper profile in the utmost toplayer of the sediments. In that case only a decrease of the input would result in decreasing contents in the sediments.
(2) to what level does the suspended solids content of the water increase and does this occur over the whole water column. Does this happen again every same storm event?

Additional fieldwork may give more information on the importance (or unimportance) of windturbation. The observed high concentrations in the south-western part of lake Westeinder, together with the fact that the waterbody in this lake is fairly well-mixed suggest fast binding processes on the toplayer of the sediments. Sedimentation of suspended solids in the inflow, due to the decrease of the horizontal velocity of the sediments is probably adding to the accumulation.

Copper also has great affinity for organisms, for organic matter and for solid phases (Leckie and Davies, 1979), in fresh water as well as in seawater. Complexation with organic suspended material and binding to the organic peaty lakebeds of lake Westeinder and lake Elfhoeven is thus very well possible, but also uptake by algae can occur. The affinity to organic material may even be the cause for the rapid binding which is very likely to occur in lake Westeinder (Salomons and Forstner, 1984). When the fine organic material is physically separated from coarser particles in the sediments, for instance due to wind, a negative correlation of copper with aluminum (clay) and silicon (sand) should result. The correlation coefficients are not significant however. An enrichment of the toplayers by a kind of filtering process then remains as possible cause. Davis (1983) and Davis and Miller (1979) suggested that activities of worms in coastal and estuarine sediment toplayers may be the mayor mechanism for the exchange of contaminants across the sediment-water interface by formation of burrow walls that provide additional sorption surfaces. Bioturbation, also described by a.o. Graneli, 1979, Gallep, 1979 and Fleischer, 1978, does not seem to be so important when looking at the high copperamounts in the toplayer.

Careful dredging of only the utmost toplayer of in fact only a few cm of the sediments at selected locations will remove a considerable amount of the copper-contents of the sediment. In lake Elfhoeven sediments such a selective dredging is not effective because of the more uniform spreading of copper in the toplayers of the sediments.

Conclusive explanations on the observed large quantity of copper can not be given so far. The observed pattern of copper suggests that further research on the sediments of both the Ringvaart canal and the lakebed for the contents, distribution and forms of copper will provide useful results: the distribution of most of the other elements (like arsenic) is merely random. The transport of sedimentary material can be studied directly by field investigation. In order to optimize that work it seems to be useful to collect copperprofiles from other selected lake-bottoms. This can provide additional information on questions like: do lakes with and without infiltration of surface water show the same profiles, always or sometimes and are there lakes where no profiles are observed. Improvement in the precision of the measurements of copper in the surface waters will probably also be effective. The water budget can also be improved which results in far more reliable estimates of the waterflow and thus of the transport processes. Measurements on the transport of material along the bottom of the Ringvaart canal and better knowledge of the turbulent exchange processes at the inflow locations of lakes and dispersion processes in these type of surface waters will also enlarge the insight in the processes that determine the observed structures of a.o. copper. These questions need answers, before extensive fieldwork with other elements will provide additional information on the processes that have lead to the observed structures in this study.

Chapter VII

DISTRIBUTION PATTERNS AND BUDGET OF PHOSPHATE IN THE SEDIMENTS

7.1 INTRODUCTION

During the last 20 years, surfacewaters in the Netherlands are loaded with considerable amounts of phosphates. The phosphate loading on the surface waters in the administration region of Rijnland is calculated from budget studies (Rijnland yearreport, 1981), amounts for 14-15 gP/m2.yr and mainly originates from two sources: wastewater discharges (over 70%) and the river Rhine (about 10%). Other sources are run off, upward percolating groundwater, inflow at locks and precipitation. 3-7 gP/m2.yr remains in the area. These figures were calculated for the whole region of Rijnland. Large differences exist between the lakes within the area (Klapwijk, 1982). Phosphate retention in lake Westeinder and lake Elfhoeven was calculated from budget studies by de Groot (1979), de Groot et al (1981), Pater (1981), Quapp (1980) and Schmidt van Dorp (1978).

In this chapter the results of a discussion on the water- and phosphate budgets of lake Westeinder and lake Elfhoeven and the observed distribution and structure of phosphate in the sediments are used for calculations on the phosphate budget in the sediments. As a consequence it was possible to compare the balancing terms of our phosphate budget of the sediments -input or output term of the sediment system- and the balancing term that results from the phosphate budget in the water. The importance of reliable water budgets clearly appeared. Inputs for sediments are outputs from the water. A correct water budget is therefore essential for calculations on transport processes across the sediment water interface. The balancing term of the phosphate budget of the water, necessarily containing all uncertainties, is often attributed to transport from or to the sediments (a.o. Grinberg, 1977, Scheiner, 1978). This way of calculation is used primarily in consequence of the lack of data from the field. Better knowledge of the composition of sediments, underlying lakes and rivers and a better understanding of transport processes across the interface as a consequence can greatly improve the accuracy of calculations on this subject. Research should in this respect aim at a reduction of routine and an increase of the recognotion and understanding of phenomena.

7.2 DISCUSSION ON THE WATER- AND PHOSPHATE BUDGET OF THE LAKEWATER

The water budget is a prerequisite for a discussion on the copper and phosphate budgets and for conclusions on the spatial structures of copper and phosphate in the sediments. Two water- and phosphate budgets on lake Westeinder were published (de Groot et al, 1979, de Groot, 1981 and Schmidt van Dorp, 1978). They used different input data and different hydrological approaches. Their approaches and accuracy are discussed.

For the Reeuwijk lake area Pater (1981) gives a detailed waterbudget. His results are used for the discussion on copper in chapter VI and phosphate in this chapter.

7.2.1 Water- and phosphate budget of lake Elfhoeven

An excellent, detailed phosphate budget based on a water budget for polder Reeuwijk that includes lake Elfhoeven was made by Pater (1981). The gross phosphate loading on polder Reeuwijk is 1.58 gP/m2.yr for 1978, 1.70 gP/m2.yr for 1979 and 1.48 gP/m2.yr for 1980.
Two output terms of the water- and phosphate budget are distinguished by Pater: the term for phosphate in downward percolating surface water (300 kgP/yr) and the balancing term for phosphate retention (5000 kgP/yr). With a total sediment area of 7.6 sqkm in the Reeuwijk lake area the total amount of 5300 kgP/yr results in an average transport rate from the water to the sediments of 0.70 gP/m2.yr.

The phosphate transport to lake Elfhoeven sediment is probably considerably higher than the above calculated average since it is the first lake in the flow system that recieves phosphate-rich water from the Breevaart canal. Moreover the lakes Broekvelden en Vettenbroek (fig 5) are not interconnected to the other lakes, thus increasing the input share of the other lakes. From the ratio of yearly average total-phosphate concentrations and the sediment surfaces in the separate lakes of the Reeuwijk lake area the loading on lake Elfhoeven was calculated by us to be about 30 % higher than the average loading on the interconnected lake area. The average loading on the sediments in lake Elfhoeven thus becomes 0.91 gP/m2.yr.

7.2.2 Water budget of lake Westeinder

Inflow and outflow in lake Westeinder occur through a complex hydrological system of connections between the lake and the Ringvaart canal shown in fig 4. Schmidt van Dorp (1978) assumed the entire waterflow in the Ringvaart canal (2 m3/s) to flow through the lake and the waterlevel in the lake to be constant. She further assumed that the whole lake volume is used for flow-through and arrived at a residence time of the water of about 5 months. Part of the water flow of the Ringvaart canal can be considered to pass the lake and will continue to flow in the Ringvaart. The residence time of 5 months must therefore be considered a lower limit. The calculated residence time increases with an increased fraction of Ringvaart canal water, not entering the lake.

De Groot et al (1979) and de Groot (1981) used daily measured fluctuations in water level in the canal to calculate the daily in- or outflow. The average residence time of the lake water is calculated as the ratio of the lake volume 25.11 millions m3 over the two output terms outflow and percolation and arrived at 10.7 months (in winter 8.3 months, in summer 13.9 months). With an assumed average waterflow in the Ringvaart canal of 3 m3/s (de Groot) it follows that an average inflow accounts for 32 ± 7 % of the total flow in the Ringvaart canal. This means that 0.95 ± 0.20 m3/s of the waterflow in the Ringvaart canal flows through the lake. This flow is about 50 % of the flow in the Ringvaart canal of 2 m3/s given by Schmidt van Dorp thus leading to a corrected residence time of Schmidt van Dorp of 10 months.

De Groot based his calculations on measurements of the water levels, as is probably better than the basic hypothesis of Schmidt van Dorp that the whole waterflow of the Ringvaart canal flows through lake Westeinder. The fluctuations in water level as used by de Groot meanwhile include fluctuations as a consequence of wind setup of the water in the lake. Next to this, the differences in waterlevel, as measured by de Groot, only include the net water exchange, but not the exchange of water due to turbulence. This might diminish the residence time of 10.7 months. 10.7 months must therefore be considered an upper limit and the residence time thus will have a value between 5 and 10.7 months. In Wit's geohydrological study of a large area in the western part of the Netherlands (Wit, 1974), the average infiltration ratio in lake Westeinder was calculated as 1 mm/d. Wit based his calculations on data of piezometric heads of the deep groundwater and the resistance of the groundlayer, that covers the aquifer. This publication was erroneously cited by Schmidt van Dorp, who used an infiltration ratio of 1.5 mm/d for her calculations. The resulting water budget is shown in table 20.

7.2.3 Phosphate budget of lake Westeinder

With the data of the water budgets the phosphate budget of the lakewater is arranged. The phosphate budgets of the lakewater as given by de Groot et al (1979), de Groot (1981) and Schmidt van Dorp, are given in table 20. The balancing term in these budgets is assumed to be the transport of phosphate to the sediments. Schmidt van Dorp used average total phosphate concentrations of Rijnland sampling points 32 and 27 situated upstream and downstream of the lake entrance in the Ringvaart canal for phosphate input and output and assumed an average flow of 2 m3/s in this canal. She estimates the net phosphate loading on lake Westeinder as [tP(32)-tP(27)] * Q * time.

Table 20.

Water and phosphate budgets in lake Westeinder

Water budget after Schmidt van Dorp (millions m3/yr)			
Inflow	63.1	Outflow	63.1
Net precipitation	4.1	Downward percolation	5.2
Unknown balancing term	1.1		
Water budget after de Groot (millions m3/yr)			
Inflow	29.5	Outflow	24.7
		Downward percolation	3.4
		Unknown balancing term	1.4
Phosphate budget after Schmidt van Dorp (tons P/yr)			
Ringvaart water	10.0	Downward percolation	4.3
Wastewater discharges	3.7	On balance remaining	9.9
Precipitation	0.5		
Phosphate budget after de Groot (tons P/yr)			
Inflow	17.28 ± 6.72	Outflow	7.44 ± 3.36
Discharges	3.72 ± 0.48	Downw. percol.	1.08 ± 0.36
Precipitation	0.36 ± 0.24	Balanc. term	12.84 ± 7.54

For the years 1979, 1980, 1981 and 1982, the average concentrations total-phosphate on sampling location 27 however are larger than on location 32 (Rijnland yearreport). From this it follows that the water coming from lake Westeinder contains more phosphate than the water flowing in, meaning a negative net P-loading of lake Westeinder. The method used by Schmidt van Dorp thus leads to errors in the phosphate loading of the lake and will therefore not further be considered.

Using the flow to the lake, calculated by de Groot as 0.95 ± 0.20 m3/s and the average total-phosphate concentrations on sampling location 32 for 1979: 0.57 gP/m3, 1980: 0.52 gP/m3 and 1981: 0.54 gP/m3 the gross phosphate loading on lake Westeinder amounts for L(P,lake) = tP(32) * (Q/A) * time. This results in gross phosphate loadings for 1979: 1.84 ± 0.39 gP/m2.yr, for 1980: 1.67 ± 0.35 gP/m2.yr and for 1981: 1.74 ± 0.37 gP/m2.yr. The yearly periodicity is not quantified here. The average is 1.75 ± 0.37 gP/m2.yr.

7.3 OBSERVED STRUCTURES IN THE SEDIMENTS

7.3.1 Horizontal phosphate patterns

Lake Westeinder

The phosphate depth profiles in lake Westeinder sediments can be separated in groups as they show different forms. In cores 1, 2, 4, 6, 7, 8, 9, 11, 13 and 14, a high phosphate concentration was observed in a toplayer with a thickness of only a few cm. In the cores 3, 5, 10, 15, 16 and 17, a phosphate accumulation to greater depths was observed. It appears that this high concentration in the toplayer correlates to some degree with the high copper concentrations in the thin toplayer in lake Westeinder sediments (cores 2, 7, 8, 9, 12, 13, 14 and 17). The two different profile forms are consistent with the differences in infiltration ratio in lake Westeinder as discussed in chapter VI. The high infiltration ratio in the south western side of the lake can prevent rapid chemical equilibrium with high sediment phosphate concentrations and can cause downward transport of phosphate. The total-phosphate concentration, increasing in deeper layers of some cores (eg. cores 5, 10, 12 and 15), do not contradict this explanation. The interstitial water concentrations however, were widely scattered and more research is necessary to quantitatively establish this qualitative relation.

Lake Elfhoeven

In lake Elfhoeven, a possible existance of horizontal structure of the data is tested for each analysed depth by trying to distinguish between groups of cores with possible other characteristics. No significant differences exist between the average phosphate concentrations in the sediments in lake Elfhoeven. If processes are active that influence the phosphate concentrations in the sediment, they results in differences that disappear in the three-dimensional distribution.

7.3.2 Phosphate depth profiles

The depth profiles of phosphate concentrations in the solid sediments show a structure at nearly all sampling locations in both lakes. This is clearly shown in chapter X, (tables interstitial water phosphate and phosphate concentration of the sediment). On most sampling locations in both lakes, the phosphate concentration in the dry sediment in the upper layer of 1 to 5 cm is high and decreases without large discontinuities with depth till a stable value is reached at depths of 30-40 cm (lake Westeinder) and 10-15 cm (lake Elfhoeven). The same was observed with the total phosphate concentrations in the interstitial water at depths larger than about 40 cm. We therefore assumed equilibrium situations at depths of 40 cm and more. Figure 18 shows the average depth profiles of sediment phosphate concentration. The total amount of phosphates in the sediments can be considered to consist of two fractions of which the second can be further splitted:

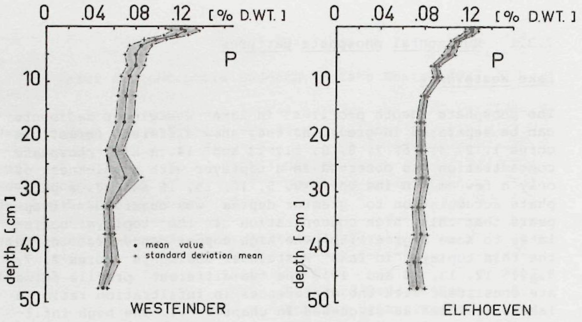


Figure 18: Phosphate depth profiles in Westeinder and Elfhoeven sediments

(1) a fraction that can be considered as background sediment phosphate. This fraction is the difference between the total amount of phosphate in the sediments and the retained amount of phosphate during the calculated period of phosphate input. This fraction is fairly large in both lakes. This can be consistent with the area around the lakes, that is eutrophic in the natural situation already.

(2a) a fraction that is homogeneously transported through the sediment. This fraction is assumed to exist, because the total amount of phosphate that is retained by the sediments, exceeds the amount of phosphate that is accumulated between the sediment-water interface and the so-called penetration depth. This fraction is roughly calculated as the difference between the phosphate input from the surface water and the amount of phosphate accumulated in the toplayers (fraction (1)).

(2b) a fraction that is bound only in the toplayers of the sediments. The limited depth to what this fraction occurs, can be looked upon as a maximum penetration depth for this fraction.

A constant phosphate retention intensity by the sediments from the water is thus assumed. The peak is described below by a linear model. This approach is used for calculations on the phosphate budget of the sediments.

From the observed phosphate depth profiles it is seen, that a more or less triangular part exists in the profiles in the toplayers of both lake-bottoms. In layers, deeper than about 30 cm in lake Westeinder and deeper than about 10 cm in lake Elfhoeven the phosphate concentration is nearly constant. This depth can be considered as phosphate penetration depth for one particular phosphate fraction. Beneath this depth a constant phosphate content is calculated as the arithmetic average of the content of the layers deeper in the sediment. In the layers from the sediment-water interface down to this equilibrium depth the exponential model is linearized and the total amount of sediment phosphate in the triangular parts of the depth profile is calculated considering the observed standard deviation (figure 19).

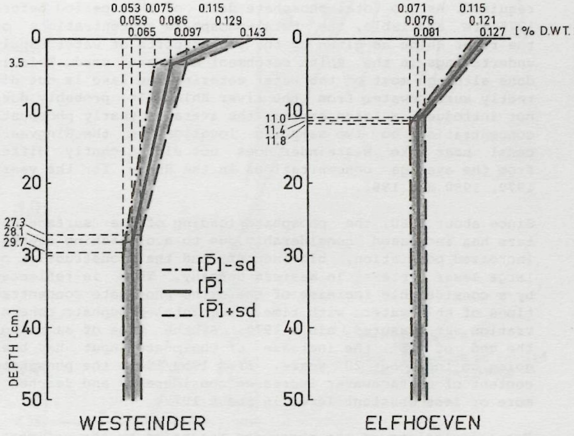


Figure 19: Phosphate depth profiles considering the standard deviations

Table 21.

Extra amount of phosphate accumulated in the toplayers

Amount of phosphate	mean - sd [tons P]	mean [tons P]	mean + sd [tons P]
lake Westeinder	129.6	189.1	261.6
lake Elfhoeven	10.8	12.1	13.4

The amount of phosphate calculated (table 21) is compared to the accumulated retention by the sediments as a consequence of the loading by the phosphate concentration of the surface water.

7.4 PHOSPHATE BUDGET OF THE SEDIMENTS

7.4.1 Phosphate loading of the sediments

When we want to discuss the phosphate content of the sediment as a consequence of *retention during* the period of eutrophication, quantitative information on the total-phosphate content of the water that flowed through the lakes is required. As no total-phosphate data of the period before 1975 are available, the total-phosphate concentrations of the river Rhine as given by the year reports of water supply undertakings in the Rhine catchment area are used. This is done although most of the water entering the lake is not directly surfacewater from the river Rhine. It probably does not introduce a large error: the average yearly phosphate concentrations on two sampling locations in the Ringvaart canal near lake Westeinder does not significantly differ from the average concentrations in the Rhine for the years 1979, 1980 and 1981.

Since about 1960, the phosphate loading of the surface waters has increased considerably due to a.o washing agents, increased population, bio-industry and the construction of large sewer systems in Western Germany. This is reflected by a considerable increase of the ortho-phosphate concentrations of Rhinewater with time. The total-phosphate concentration was measured since 1972. At the time of sampling, the end of 1981, the increase of phosphate input had been going on for about 20 years. From 1959/1960, the phosphate content of surfacewater increased considerably and reached a more or less constant level in about 1972.

For calculations on the phosphate retention by the sediments and their phosphate contents as a consequence, the gradually increasing total-phosphate discharge of the river Rhine is graphically schematized to an instantaneous increase. This is done in two steps. First, a linearisation of the increase of the total-phosphate concentration is made that next is transformed to a step increase. Graphically this is done by equalizing the surfaces a and b in fig 20.
This results in an assumed sudden increase of the total-phosphate discharge of 1.37 kgP/s, entering the Netherlands with the water of the river Rhine in 1966. Two periods of time can now be distinguished, separated by the first of january 1966: low phosphate input before this date and increased input afterwards. According to this schematization, it is assumed that we know the loading course from 1966 to the time of sampling, 16 years later.

Now, we have established two basic needs for a quantitative phosphate budget in the sediments:
(1) the amount of phosphate in the accumulations in the toplayers of the sediments that can be considered as an enrichment due to eutrophication and
(2) the time and intensity of the eutrophication

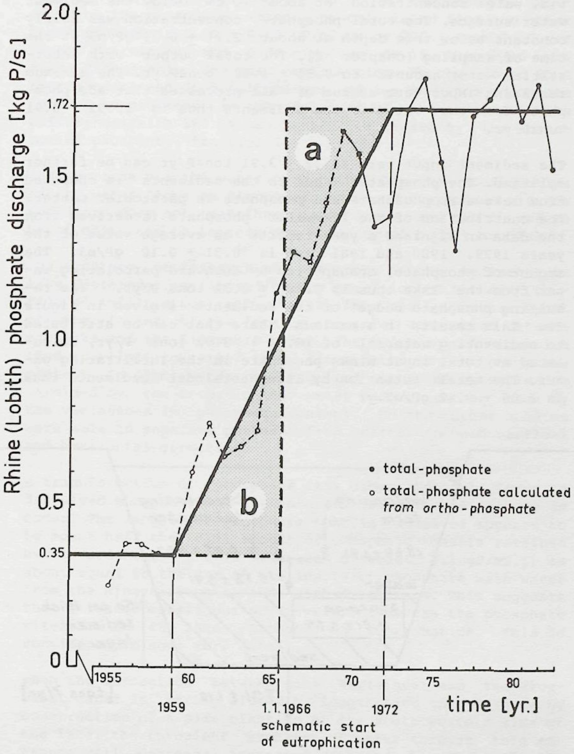


Figure 20: Graphic determination of the phosphate retention period

7.4.2 Phosphate budget of lake Westeinder sediments

A sediment layer *of about 40 cm thickness* is considered as black box system. In this layer at least 189 ± 60 tons of extra P are stored (table 21) during the input period of 16 years or 11.81 ± 3.75 tonsP/yr. Output from the sediment black box-layer *occurs through downward* percolating water. The average total-phosphate concentration of this percolating water (1 mm/day) is assumed to be equal to the interstitial water concentration at about 40 cm below the sediment water surface. The total-phosphate concentration was fairly constant below this depth at about 2.21 ± 0.33 gP/m3 at the time of sampling (chapter X). The total output with interstitial water amounts to 7.51 ± 1.12 tonsP/yr. The maximum resulting input term as sum of all processes that add phosphate from the water to the sediments thus is 19.32 ± 3.91 tonsP/yr.

The sediment input term 19.32 ± 3.91 tonsP/yr can be further splitted. The phosphate input to the sediments is composed from lakewater phosphate and phosphate in particular matter. The contribution of the lakewater phosphate is derived from the data in Rijnland's year-reports as average value of the years 1979, 1980 and 1981 and is 0.31 ± 0.10 gP/m3. The amount of phosphate, transported by downward percolating water from the lake thus is 0.98 ± 0.32 tons P/yr. The resulting phosphate budget of the sediments is given in figure 21. This results in a maximum share that can be attributed to sedimenting material of 18.34 ± 3.92 tons P/yr, calculated as total input minus phosphate in the infiltrating water. The total retention by lake Westeinder sediments thus is 2.08 ± 0.42 gP/m2.yr

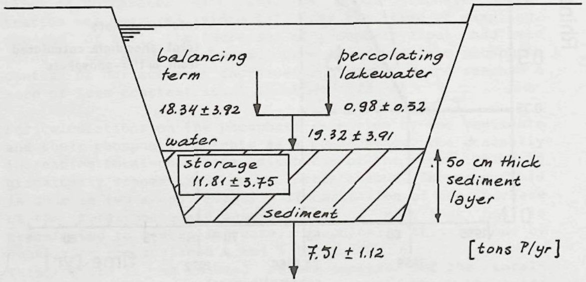


Figure 21: Phosphate budget of the sediments in lake Westeinder

The separate shares of phosphate transport to and through the sediments are calculated without using the balancing term from the water- and phosphate budget (table 20). This allows comparison with de Groot et al. The maximum yearly phopspate input of the sediments of 19.32 ± 3.91 tons P/yr, being the input calculated from the data in the sediments, is higher than the phosphate transport to the sediments of 13.92 ± 7.53 tonsP/yr (de Groot et al) but the results roughly correspond within the uncertainties. These include

fraction (2a), as decribed in 7.3.2. In the observed layer of 40 cm the phosphate retention, calculated from the other budgetstudies is 1.50 ± 0.81 gP/m2.yr or 223 ± tons P/16 yrs (lake Westeinder) and 0.91 gP/m2.yr or 16 tons P/16 yrs (lake Elfhoeven). See also next section. We thus found 85 % (Westeinder) and 76 % (Elfhoeven) of the retained phosphate to have accumulated in the toplayers of the sediments. The differences with 100 % can partly be caused by the transported phosphate, fraction 2a.

The approach via the water budget includes the uncertainties of the water flows as discussed above. The approach via the sediments does not use these water flows and can therefore be of great use to improve the accuracy of budget studies.

The accuracy of research on phosphate in the sediments in lake Westeinder is limited by the precision of the distribution of infiltration ratios in the lake and by the transport of water in and out the lake by the inlet connection between the lake and the Ringvaart canal. The hydrological situation thus is limiting rather than the scatter in the phosphate content. In other words: the required number of cores is determined by the error in the water budget, rather than by the variations in phosphate content. On the other hand we were able to separate patterns from scatter in both vertical and horizontal direction.

A transformation of phosphate from other chemical forms to dissolved phosphate in the interstitial water is likely to occur. The amount of phosphate that is involved appears to be about half the total amount of phosphate that is retained by the sediments. This retention of about 2.1 gP/m2.yr is about equal to the sum of the inputs of phosphate with water from the Ringvaart canal and with discharges. This suggests that a lesser waterinput positively influences the phosphate situation in the lake, probably at short notice. This is considered in some more detail.

When the connection between lake Westeinder and the Ringvaart canal is partly closed by lengthening the dyke or by construction of a pile planking at the south western side of the lake, the turbulent exchange of water through this entrance will decrease. Increased retention by the sediments will result in decreasing phosphate contents of lake Westeinder. In the sediments this must result in depth profiles, with diminishing accumulations in the toplayers. It should be possible to follow this process with a sampling program in water and sediments with sampling frequention of a few months.
The free exchange of water between the lake and the Ringvaart as a consequence of differences in water level, as well as free entrance of boats, meanwhile, are not prevented or hindered. A dam and/or an artificial isle, thus will not disturb the quantitative water management and may contribute to the qualitative one.

In principle, we expect a similar effect with copper. The processes may also be monitored by a sampling program and may give more information on the transport rates involved.

For the copper budget these measurements may have the additional advantage, that the possible copper transport mechanism, rolling material on the bottom of the Ringvaart canal that enters the lake in the south western part, is controlled almost entirely. It may also have positive effects on the inputs of other metals into the lake.

7.4.3 Phosphate budget of lake Elfhoeven sediments

The phosphate budget of lake Westeinder sediments is based on the inflow of lakewater and outflow to deeper groundwater of interstitial water. In lake Elfhoeven the ratio of infiltration of lakewater through the sediments is only 0-0.25 mm/day (Wit, 1974). Therefore we were not able to make the same calculation for lake Elfhoeven sediments as we did for lake Westeinder sediments.

Our calculations on the accumulations in lake Elfhoeven sediments are very well consistent to *the much smaller infiltration* ratio of water through lake Elfhoeven sediments. The calculated phosphate retention of 0.91 gP/m2.yr results in a retention of 16 tons P during the 16 year input period. The phosphate accumulation in the toplayers was calculated as 12.1 ± 1.3 tons P (table 21). The observed accumulation thus accounts for about 76 ± 8 % of the total input during *the assumed input period of 16 years as already indicated in* 7.3. This percentage is about the same as the part of the input that was found in the toplayers of lake Westeinder sediments. With the uncertainties in the data used for this calculation, the phosphate input into both lake sediments during the input period of 16 years is about quantitatively found in the toplayers of the sediments.

The calculated retention of 0.91 gP/m2.yr probably only contains a small error. This error is estimated to be around 10 %. The period of 16 years only includes a deterministic non statistical error introduced by the schematization of fig. 20. It is also estimated to be about 10 %. This error in the amount of phosphate that is transported to the sediments in lake Elfhoeven thus contains an error that can be estimated about 15 %.

This is consistent with the much smaller infiltration ratio in lake Elfhoeven and with the depth profile of the total-phosphate concentration in lake Elfhoeven sediments that shows nearly constant concentrations deeper than about 10-15 cm depth (chapter X). In lake Westeinder sediments the total-phosphate concentration stabilizes only at depths of about 40 cm.

These results clearly indicate that, as far as lake Elfhoeven is concerned, the phosphate budget of the water made by Pater (1981) and the phosphate budget of the sediments as calculated by us agree very well with respect to the transport of phosphate across the sediment-water interface. This means that the data used for both budgets can be used in further research on this subject without introducing large uncertainties or errors.

7.5 RETENTION AND TRANSPORT OF PHOSPHATE IN SEDIMENTS

7.5.1 Phosphate retention by the sediments

Following to the schematic phosphate discharge of the river Rhine and the calculated period of input of phospates (preceeding section), it is assumed that we know the loading course of the lakes from 1966 to our sampling in 1981, 16 years later. A difference was observed between the retained phosphate and the phosphate loading in both lakes (section 7.4.1). If the loading was overestimated the toplayer contains a larger percentage of the total retained phosphate. Ortho-phosphate data of the river Rhine from 1945 indicate *that the schematization is about correct.* Transport of a part of the retained phosphates through the sediment to deeper layers can have occured, especially in lake Westeinder with its relatively high infiltration ratios. If it is assumed that this fraction is homogeneously spreaded in the layer with a thickness of 50 cm, it can be substracted from the observed depth independent phosphate fraction. The remaining fraction *can now be considered as phosphate content* that is present as natural value in both lakesediments.

The phosphate profile in the sediment can pass several stages when phosphate is transported to the sediment during a long period of time. The original not eutrophicated situation can be represented by vertical lines as depth profiles. Increasing eutrophication results in the profiles that were observed in the lakes. The depth profile can develop further, dependent on the adsorption and exchange capacities of the sediments or show saturation like ion-exchangers do. This results in profiles that show a constant high value to a limited depth, followed by a decrease. Such depth profiles were observed in sediments in the Andelse Maas Basin where considerable additions -iron and phosphates together with sedimenting material- to the sediments occur, as is described below. Release or remobilization of phosphate can occur when the adsorption capacity is exceeded, resulting in a concentration decrease in the toplayers again. The differences, developing as a consequence of sediment characteristics, can be described with a simple model, that expresses the loading in the past:

$SL(P,p) = [P(p)] * Q(p)/A(p) * r(p)$ and the loading now:

$SL(P,n) = [P(n)] * Q(n)/A(n) * r(n)$ in which:

$[P(n)] = [P(p)] + [P(e)]$

Symbols and indices are:

$[P(n)]$ = lakewater phosphate conc. now [gP/m3]
$[P(p)]$ = lakewater phosphate conc. in the past [gP/m3]
$[P(e)]$ = increase of phosphate conc. (step) [gP/m3]
Q = waterflow [m3/yr]
A = surfacearea of the sediment [m2]
$SL(P)$ = phosphate loading of the sediment [gP/m2.yr]
r = retention factor of the sediment [-]

p = past: before stepwise increase [-]
n = now: after stepwise increase [-]
e = extra: the stepwise increase [-]

It is assumed that the waterflow and the surfacearea did not change. Reliable hydrological models may improve this assumption. The error in the phosphate concentration originates from the analysing techniques and has to be accepted for the time being. The retention of phosphate by the sediment then is in fact the only balancing term in the budget models presented. This factor will be discussed in some more detail.

As first approximation it is assumed that the retention does not change with time: $r(p)=r(n)$. The retained amount of phosphate is now only dependent on the phosphate concentration of the overlying lakewater.
Some qualitative considerations can be given on the model, when applied to some cores, taken from the sediments of the Andelse Maas Basin. This is a surface water in the Netherlands that connects the rivers Rhine and Meuse. Surfacewater from this basin is withdrawn by the watercompany of the city of the Hague. In 1904 the open connection was closed by building a shiplock. Two hydrological different situations are defined now, the situations before and after the shiplock was build. Before 1904 the phosphate loading of the sediments in the basin can be calculated as:

$$SL(P,p) = [P(p)] * Q/A * r(p)$$

This input could not be traced in the sediments (de Kruijk et al, 1984). From 1960, the phosphate concentration in the Rhinewater increased and the input can be described as:

$$SL(P,n) = ([P(p)] + [P(e,t)]) * Q/A * r(p)$$

in which $[P(e,t)]$ is the time-dependent increase of the total-phosphate concentration in the surfacewater From 1976, phosphate is removed from the water in this basin, resulting in a sediment input model:

$$SL(P,t) = ([P(p)] + [P(e,t)]) * Q/A * [r(p) + r(e)]$$

In this model an increase of the retention to $r(p)+r(e)$ is taken into account. The extra retention $r(e)$, can occur due to an accumulation of sedimenting material. This results from precipitation and co-precipitation as a consequence of the chemical phosphate reducing activities by the watercompany.

The hypothesis of a retention that varies with time and location can be illustrated from the depth profiles of lake Westeinder and lake Elfhoeven on the one hand and those of the sediments in the Andelse Maas Basin on the other hand. Those in the lakes are hollow-shaped: the largest values are measured in the utmost toplayer. Those in the basin are spherically shaped (de Kruijk et al, 1984) and the largest values are measured at depths of 5-20 cm. This difference may be caused by the dosage of ferro-sulphate (Fe(II)SO4) for phosphate removal. The binding of phosphate on the sediments most probably is different, and may be stronger when more iron is present. This chemical binding originates from the waterphase as the mechanism of phosphate removal from the surface water. The phosphates precipitated since the watercompany started the removal of phosphate in the basin in 1976, is only transported through the sediments to depths of 15-20 cm. This means that the vertical transport rate of phosphate through the sediments does not exceed 2-3 cm/yr, probably even smaller while it is expected that the sediment layer expands in upward direction as a consequence of the precipitation. It may therefore very well be that the mobility of phosphate as part of the compounds in the sediment in the Andelse Maas Basin, is smaller than in the sediments of lake Westeinder and lake Elfhoeven, which can mean that the fraction exchangeable phosphate could also be smaller. The expected difference in mobility is consistent with the existence of a phosphate fraction in the lakes, that is transported through the sediment to deeper layers. These predictions and quantitative tests of the developed model are directly open to experimental tests.

7.5.2 Discussion on phosphate transport through the sediments

When the infiltration ratios on different locations in the lake are well known, the phosphate transport from the lake to and transport through the sediments can be reliably calculated. The variation of the infiltration ratio over the lake and possible variations with depth are unknown. In deep sediment layers the phosphate transport can probably be more easily calculated as bioturbation is zero and the rate therefore is the process-rate of phosphate transport. In the toplayers the contributors to the actual concentrations a.o bioturbation, the influence of the surface water and of the sediment must be split up.

In several cores the total-phosphate concentration in the interstitial water in the toplayer of the sediment column is lower than in deeper layers. This can be caused by a temporal release of phosphate to the overlying water and/or by bioturbation. In most cores steep gradients are observed in the total-phosphate concentration of the interstitial water at different depths. These high gradients can induce transport of phosphates to other layers and/or precipition in the layers itself. If this transport occurs and the profile is assumed to exist for some time, the phosphate content of the sediment of the subsequent depth layer increases. The ob-

served phosphate depth profiles are the result of transport to deeper layers through the waterphase, integrated over a long period of time. A steep slope in the total-phosphate concentration profile of the interstitial water meanwhile can indicate a local discontinuity in the ratio of transport of the water. The binding or release mechanism of the sediment works together with a transport mechanism through the sediments. Some calculations have been made on time-scales of the transport processes. The transport mechanism in this model is replacement of total-phosphate from the solid phase in layer i to layer i+1. It is assumed, that phosphate *transport only occurs with the interstitial water.* T(i) is now defined as the time required for deposition of all phosphate, present in the underlying (i+1)th sediment layer with the total-phosphate concentration of the infiltrating water from layer i as a source. The direction of transport of total-phosphate is the same as the direction of flow of the infiltrating water. In principle every observed concentration peak in the profiles can be treated this way, leading to a distribution of T(i).
The average time, required for the deposition of the phosphate in a sediment layer of 1 cm thickness, with the interstitial water phosphate as an assumed constant source is now calculated to be 1.33 ± 1.23 year in lake Westeinder and *3.16 ± 2.00 year in lake Elfhoeven sediments.* This is a fairly long period but the amount of phosphate in the sediments can be several orders larger than the phosphate concentration of the water. This is also reported by Wetzel (1975).

The calculated data give an estimation of the upper limit of the time of existance of the interstitial water profiles. It is not the maximum possible time however. Bioturbation reduces gradients and thus also reduces the calculated times of existance. To what extent is unknown. From other parts of this work it can be concluded that the dispersion effects of ao. bioturbation are most probably small (eg chapter VI). *The gradients,* assumed to be constant during the build up time, probably change considerably. How fast however, is still unknown.

The discontinuities in the depth profiles thus seem to move in vertical direction. If they vary within a short period (a few months), and some do, than it is not to be expected that cores taken on the one side of the lake correspond with cores on the other side. Time variations of a half to some years, as mostly in our work, include the possibility for comparison the one side of the lake with the other. As the discontinuities change with time in vertical direction, the concentration peak in the interstitial water is a snapshot of the differences in the concentrations in the sediment itself.

Transport processes occur with a time-scale of several years. A larger ratio of infiltration shortens this process time to some months. This is possible as can be seen in the depth profiles of the total-phosphate concentration of the interstitial water, where the largest peaks occur at depths of 30 to 40 cm (cores 5, 12, 14, 19 and 22) and 20 to 30 cm

(cores 10 and 17) as well as the sediments from 10-20 cm (cores 16, 18 and 21) and from 0 to 10 cm (cores 1, 6, 7, 8, 9, 11, 13, 15, 20, 23, 24, 25, 26, 27, 28 and 30). Influencing factors are:
(a) the ratio of infiltration (or upwelling)
(b) the storage capacity of the sediments
(c) the waterdepth and the atmospheric conditions (eg. wind causes some resuspension)

Some remarks can be made on the results of this calculation.
(1) it is assumed that the total-phosphate from the interstitial water is exclusively deposited *in the underlying* layer. If this assumption is incorrect, as is probably the case, some possibilities can be considered all resulting in a larger time scale:
(a) The total-phosphate concentration of the interstitial water can consist of two fractions, a fraction that can be ad/absorbed and a fraction that can not. Only the first fraction will be retained by the sediments. Our measurements do not allow further distinction between these two fractions.
(b) When ad/absorption takes place over more than one underlying sedimentlayer, the total-phosphate, present in the layers i-1, i-2 etc. is also deposited in the layer i+1. As quantities are largely unknown, this effect is not *taken* into account.
(c) Aging of the sediment results in a smaller adsorption capacity. Due to increasing polymerisation a displacement of the adsorption isotherm is seen (Lijklema, 1977 and 1979). The mechanisms involved are largely unknown, however.

(2) During the transport of phosphate from one layer to an other additional dispersion will occur. This causes spreading of the element over larger areas. It is assumed that the contributions of all locations around the cores and from the core to its surrounding nullify each other. In fact this means that the core is considered to represent that area, as is implicitely assumed earlier.

Transport models are often based on assumptions about the exchange of phosphate between the solid phase and the waterphase (equilibrium principle) and assume either steady state or dynamic situations (Effler et al, 1982). Some examples are Kamp-Nielsen, 1975a and 1977, Yoshida, 1981, Moller Andersen, *1975,* Moshira and Crumpton, *1978* and Jacobsen, 1978. Modelling of sorption sometimes succeeded on the phenomenological level, but mechanisms are not elucidated (a.o. Berkheiser, 1980). Discrepancies between modelsystem and fieldsituation cause errors in the predictions. The processes, that for instance cause release of phosphate in summer, are not sufficiently known. Further research and combination of model approach and simultaneous field work will probably provide more reliable information in future.
Model approaches must be based on reliable assumptions and measurements on chemical and microbiological processes, that are time-dependent as well as location-dependent. Longlasting measurements on many locations are often necessary, for instance with equipment that determines porewater concentrations by the diffusion principle with in situ equilibrium

devices, also called peepers (Adams, 1982, Brinkman et al, 1982). These methods, however, are time consuming and often demand specific equipment and/or the aid of divers.
The lack of regularity in depth structure of profiles, observed so far by several authors, makes it very difficult to model the transport of the interstitial water phosphate, as long as the processes, that cause the observed concentrations are insufficiently known. In these types of lakes the stochastic characteristics strongly dominate.

Basicly, it can be concluded that sediment total-phosphate is a far better indicator than interstitial water phosphate, because it varies less than the highly fluctuating porewater phosphate concentration. For further research on interstitial water a time resolution can be suggested of weeks or months, rather than years, because the peaks probable change in that time interval. A hypothesis for the changing interstitial water concentrations is that the decrease of a phosphate peak can be the reason for the 'growth' of a new peak.

Chapter VIII

DESIGN OF A SAMPLING STRATEGY FOR LAKE-BOTTOMS

8.1 INTRODUCTION

Research programs that include (routine) sampling of lake sediments are often based on one or very few sediment samples. The number of samples taken is often not directly related to the dimensions of the lake and the concentrations that can be expected. It is difficult to take the correct number of samples. When the sample-size is too small, wrong conclusions can easily result. When too many samples are taken, the sampling program was too expensive. This must both be avoided. The problem is: what samplesize represents the lakebed sufficiently for a given purpose.

The only way to get a perfect insight in the contents of the sediment, would be to examine the whole sediment body using a perfect analytical procedure, but is impracticable. Sufficient information about the composition of bottom sediments can be achieved by analyzing a sample of sufficient size. Due to lack of information about the variation in the concentrations the word sufficient generally can not directly be translated to a sample-size.

From our calculations it appears that, to maximize efficiency, a sampling program can best be executed in two steps. The first step of say, 6 cores, gives an impression of the composition of the lakebed through an average concentration and a standard deviation. For some elements these 6 cores will appear to be a sufficient sample size. For other elements it indicates the lack of information. The additional information can be obtained in a second sampling step. Procedures are described in this chapter. The preliminary sampling program is carried out, selecting the sampling points with the help of maps and earlier work (Paris and Verboon, 1974). The number of 17 and 13 sampling points in lake Westeinder and lake Elfhoeven resulted in an average area per sampling point of 0.55 km2 and 0.08 km2 resp. This area per sampling location is not very large in comparison to other fieldwork (table 22) because the bottom sediments in the deltaic area of the western part of the Netherlands were expected to be rather inhomogeneous.
In order to discover and describe existing spatial structures in the sediments, both horizontal and vertical, the measured data were ordered in different ways (chapter V). The concentrations of the elements and compounds were also compared with geological maps of the surrounding area of both lakes and with the composition measured by Paris and Verboon (1974). Attempt have been made to trace any kind of difference between groups of cores within the lakes.

Table 22.

Covering areas per sampling point

lake	sampling points		reference
	number	area (km2)	
Bryrup Langso (DK)	4	0.01	Moller Andersen (1974)
Esrom (DK)	1	17	Kamp-Nielsen (1974)
Fureso (DK)	1	9	Kamp-Nielsen (1974)
Granelangso (DK)	1	0.11	Kamp-Nielsen (1974)
Halla So	3	0.1	Moller Andersen (1974)
Kul So	3	0.06	Moller Andersen (1974)
Kvind So	3	0.05	Moller Andersen (1974)
Norrviken	13	0.1	Ulen (1978)
Salten Langso	5	0.6	Moller Andersen (1974)
St Gribso (DK)	1	0.1	Kamp-Nielsen (1974)
Stigholm So	3	0.1	Moller Andersen (1974)
White lake (USA)	2	5	Freedman & Canale (1977)
White lake (USA)	2	5	Lung et al (1976)
Lake Elfhoeven	13	0.08	Siebers (1982)
Lake Westeinder	17	0.55	Siebers (1982)

If the data correspond to any soil map they can not be considered as taken randomly and they can not be treated statistically. It appeared that no obvious correspondence with soil maps or geological maps existed. Apart from the distribution of copper and phosphorus no distribution pattern for the measured elements was observed. The lack of significant relation between element concentrations in the lakebed to any existing soil structure allows us to treat the data as statistical, in principle.

8.2 CALCULATION OF THE REQUIRED SAMPLE SIZE FROM THE DATA

Average concentrations and standard deviation of the data were operated with formulas from Elliott (1977) and Southwood (1978). After rearrangement the required sample-size n (*the number of cores to be taken*) is calculated from (1) the observed average concentration of the data, x(av) (2) the standard deviation of the sample, s and (3) an accepted error in the average value, E.

Further details were reported in chapter III. The required sample-size n is:

$$n = \frac{(s)**2}{[E/100 * x(av)]**2} \qquad (9.1)$$

This calculation is done in two ways: (1) an approach for the lake as a whole, using the average concentrations of the entire, 50 cm thick sediment layer and (2) an approach in which the required sample size is calculated for five different depths in the sediment.

Approach for the sedimentlayer of 50 cm thickness

To get a first impression of the required sample size, the average concentrations of the elements in the two lakes are used to calculate the required number of samples when a certain error in the result of the statistical prediction is accepted. A rank order can now be made of the required sample-sizes for the elements in a sediment layer with a thickness of 50 cm. The accepted error still has to be chosen. Reynoldsen (1982) calculates sample sizes for the Canadian lake Wabamun and chooses an error estimation of E=5 %. Due to the very uniform sediment this results in a small required number of cores. Southwood also states that 5 % error of the mean is satisfactory for many purposes. In the situation in the Netherlands the error to be accepted has to be larger as appears from table 7 in chapter V. Elliott (1977) considers an error of 20 % in the average as reasonable for soil samples.

Two sources of stochastic errors are combined in E, analytical errors that in our work vary from 1.8 % to 4.1 % and errors due to inhomogeneities in the sediment, estimated to be 10 %. The error E now becomes:

E = Sqrt [(4.1)**2 + (10)**2] = 10.8 %.

When larger errors are accepted, smaller required sample-sizes result. For calculations with average values, errors of 10 % and 20 % of the samplemean are both evaluated. The resulting required sample sizes are summarized in table 23. It can be seen from this table that most elements need large sample-sizes, if an error of 10% in the sample-mean is accepted. Especially in lake Westeinder sediments this is the case. The calculation gives information about average concentrations in the whole lakebed and will therefore also be done for each of the 5 analysed depths in the sediments.

Approach for different depths in the sediment

Here, the required sample-size is calculated for each horizontal sediment layer. Purpose of this calculation is a prediction of the required sample-size. This estimation after a limited preliminary sampling is a useful tool to keep the sampling program as restricted (and cheap) as possible. Results of this calculation are given in the tables 24 and 25. The sample-size of the taken sample n does not in all cases suffice the calculated sample size. sample-sizes' With an accepted error of 10 %, over 70 % the taken sample in lake Westeinder sediments appears to be to small. All layers show the same picture. In lake Elfhoeven the sample size was insufficient for about 40 % of the elements. When an error of 20 % in the sample mean would have been accepted the majority of the sample sizes is sufficient.

Table 23.

Required sample sizes in lakes Westeinder and Elfhoeven

Required sample-size calculated with errors in the mean of 10 and 20%. The sample-sizes taken in the field are 85 (17 cores of 5 slices each) and 65 (13 cores) resp. for both lakes.

Lake Westeinder			Lake Elfhoeven		
	accepted error in the sample-mean			accepted error in the sample-mean	
	10%	20 %		10%	20%
Al	64	16	Al	12	3
As	100	125	As	100	25
Ca	39	10	Ca	6	1
Co	44	11	Co	16	4
Cr	5	1	Cr	1	1
Cu	115	29	Cu	36	9
Fe	22	5	Fe	3	1
K	14	4	K	7	2
Mg	105	26	Mg	25	6
Mn	25	6	Mn	6	2
Ni	25	6	Ni	11	3
P	35	9	P	8	2
Pb	81	20	Pb	131	33
Si	9	2	Si	3	1
Sr	5	1	Sr	2	1
Ti	69	17	Ti	8	2
Zn	73	18	Zn	44	11
oPw	124	31	oPw	100	25
tPw	105	26	tPw	77	19
H2O	2	1	H2O	1	1

8.3 PREDICTION OF THE REQUIRED SAMPLE SIZE

8.3.1 Statistical background

In order to obtain information about a population (in this study the population of concentrations of a certain element in the sediments of a lake) a sample can be taken at random. As the population standard deviation (sigma) is not known in most geochemical and ecological investigations, this parameter is often replaced by the sample standard deviation s. The size of the sample n plays an important role in the accuracy of s as an estimation of sigma. Whether or not the average of the sample equals the population average can be tested with the Student's t-test. This test is especially suited for statistics of small samples.
In the test of the average mu of a population which is assumed to be normally distributed with unknown variance (sigma)**2, the quantity t is given by the equation:

Table 24.

Sample-sizes lake Westeinder

The required sample-sizes, dependant on the accepted error E in the mean. n is the size of the sample taken in this work.

	0-1 cm			4-6 cm			8-10 cm			25-30 cm			45-50 cm		
	E (%)			E (%)			E (%)			E (%)			E (%)		
	10	20	n	10	20	n	10	20	n	10	20	n	10	20	n
Al	37	9	14	17	4	14	23	6	14	104	26	15	139	35	16
As	100	25	15	44	11	14	44	11	14	44	11	15	100	25	16
Ca	16	4	15	16	4	14	18	5	14	22	6	15	18	5	16
Co	100	25	15	44	11	14	44	11	14	44	11	15	100	25	16
Cr	1	1	15	2	1	14	2	1	14	2	1	15	16	4	16
Cu	1	1	15	21	5	14	21	5	14	2	1	15	8	2	16
Fe	17	4	15	38	9	14	29	7	14	12	3	15	19	5	16
K	3	1	15	8	2	14	3	1	14	19	5	15	29	7	16
Mg	593	148	15	66	16	14	41	10	14	80	20	15	67	17	16
Mn	40	10	15	35	9	14	33	8	14	11	3	15	18	5	16
Ni	25	6	15	25	6	14	25	6	14	25	6	15	100	25	16
P	19	5	17	31	8	17	18	5	17	61	15	17	15	4	16
Pb	400	100	15	100	25	14	62	15	14	18	5	15	40	10	16
Si	6	2	15	8	2	14	4	1	14	10	3	15	15	4	16
Sr	6	1	15	4	1	14	5	1	14	6	2	15	7	2	16
Ti	62	15	15	87	22	14	74	18	14	73	18	15	120	30	16
Zn	167	42	15	64	16	14	67	17	14	38	10	15	50	12	16
oPw	28	7	16	83	21	17	158	40	17	119	30	17	48	12	16
tPw	49	12	15	85	21	17	94	24	17	143	36	15	124	31	16
H2O	2	1	17	3	1	17	3	1	17	2	1	17	1	1	16

$$t = \frac{x(av) - mu}{s/sqrt\ n} \qquad (9.2)$$

t is defined to be the deviation of the estimated mean from the population mean in terms of s/sqrt n as the unit (Snedecor and Cochran, 1967). The distribution of this stochastic variable t (in large samples: mu = 0 and sigma = 1) can be calculated from x(av) and s of the sample. If the sample-sizes are less than 30, the distinction between sample and population becomes obvious. The t-distribution is symmetrical about the mean. The distribution of the concentrations of the elements can be considered as standard normal. In most cases, the assumption is justified (Siebers, 1982). Therefore, no transformations of any kind were executed. The null-hypothesis H(0) : mu = x(av) can now be tested by using the existing tables of the Student distribution. When alpha is the chance that the average of a new sample will be larger than R2 or smaller than R1, rejection of the null-hypothesis will occur for values of mu:

$mu \leq x(av) - t[(1/2\ alpha),(n - 1)] * s/sqrt(n)$ or

Table 25.

Sample-sizes lake Elfhoeven

The required sample-sizes, dependant on the accepted error E in the mean. n is the size of the sample taken in this work.

	0-1 cm			4-6 cm			8-10 cm			25-30 cm			45-50 cm		
	E (%)			E (%)			E (%)			E (%)			E (%)		
	10	20	n	10	20	n	10	20	n	10	20	n	10	20	n
Al	17	4	11	6	1	13	6	2	13	10	3	13	21	5	12
As	278	69	11	44	11	13	44	11	13	44	11	13	100	25	12
Ca	1	1	11	1	1	13	1	1	13	5	1	13	5	1	13
Co	16	4	11	4	1	13	16	4	13	25	6	13	25	6	12
Cr	1	1	11	1	1	13	1	1	13	1	1	13	1	1	13
Cu	14	3	11	6	2	13	25	6	13	6	2	13	6	2	12
Fe	1	1	11	3	1	13	4	1	13	2	1	13	8	2	12
K	1	1	11	2	1	13	4	1	13	10	3	13	16	4	12
Mg	117	29	11	8	2	13	10	2	13	17	4	13	21	5	12
Mn	13	3	11	6	1	13	3	1	13	4	1	13	6	2	12
Ni	11	3	11	11	3	13	11	3	13	11	3	13	11	3	12
P	19	5	13	31	8	13	18	5	13	61	15	13	15	4	12
Pb	400	99	11	128	32	13	11	3	13	158	40	13	34	8	12
Si	1	1	11	1	1	13	1	1	13	6	1	13	8	1	12
Sr	1	1	11	1	1	13	1	1	13	3	1	13	5	1	12
Ti	5	1	11	9	2	13	9	2	13	9	2	13	9	2	12
Zn	144	36	11	8	2	13	11	3	13	63	16	13	30	8	12
oPw	102	25	13	195	49	13	108	27	13	76	19	13	54	14	12
tPw	75	19	12	130	33	13	69	17	13	54	13	13	33	8	12
H2O	1	1	13	1	1	13	1	1	13	1	1	13	1	1	13

$$mu \geq x(av) + t[(1/2\ alpha),(n - 1)] * s/sqrt(n)$$

In this way two critical values can be calculated. Two var*iables influence the prediction of x(av) of the new sample* (1) the required confidence interval of the prediction and (2) the size of the new sample.
When the confidence interval of the prediction is chosen t *follows from the tables of the Student-distribution and the* size of the first sample. R1 and R2 as the limit values can be calculated as a function of the size of the new sample n(new), while s is also known from this first sample. Thus: *R1 = f [n(new)] and R2 = f [n(new)]*

It is clear that an increasing n(new) results in a decreasing range in the prediction of the average of this new sample. *These predictions of sample sizes are made below.* The prediction can be approached from two sides:

(A) When a new sample with a size n(new) is taken from the lakesediments, the predicted sample mean lies between two limit values that can be calculated: *R1* and R2. The confidence interval of this prediction is known: CI %.

(B) When an error in the population mean of E % is accepted, the size of the sample, which should have been necessary, on the basis of the measurements, can be calculated.

<u>ad</u> (<u>A</u>)
The confidence interval of the prediction (CI) and the size of the new sample n(new) are conflicting parameters:

(1) When a prediction is made with a certain confidence CI, an increasing n(new) narrows the range of the limit values of the predicted average x(av)
(2) When a prediction with a chosen sample size n(new) is made, an increasing confidence interval widens the range of the predicted averages of the new sample.

From this it is clear that a conflict is arising between the statistical and the management point of view: from the managing point of view a large confidence interval of the prediction should be coupled to a sample size as small as possible (and thus as cheap as possible). A more reliable prediction in statistical terms corresponds with a larger sample size.

<u>ad</u> (<u>B</u>)
When an error in the population mean of E % is accepted, the null - hypothesis H(0) : mu = x(av) is accepted when

$$x(av) \leq \frac{100 + E}{100} * mu$$

or

$$x(av) \geq \frac{100 - E}{100} * mu$$

both preceeding equations can be rewritten as

$$mu \geq \frac{100}{100 + E} * x(av) \qquad (9.3)$$

and

$$mu \leq \frac{100}{100 - E} * x(av) \qquad (9.4)$$

the quantity t is given by the equation

$$t = \frac{x(av) - mu}{s\ /\ sqrt\ n} \qquad (9.5)$$

which can be rewritten to

$$mu = x(av) - \frac{s * t}{sqrt\ n} \qquad (9.6)$$

Elimination of mu from the equations (9.3) and (9.5) results in

$$x(av) - \frac{s * t}{sqrt\ n} \geq \frac{100}{100 + E} * x(av) \qquad (9.7)$$

Elimination of mu from the equations (9.4) and (9.6) results in

$$x(av) - \frac{s * t}{sqrt\ n} \leq \frac{100}{100 - E} * x(av) \qquad (9.8)$$

Equation (9.7) can be rewritten to

$$sqrt\ n \geq \frac{s * t}{[E / (100 + E)] * x(av)} \qquad (9.9)$$

and (9.8) to

$$sqrt\ n \leq \frac{s * t}{[E / (100 - E)] * x(av)} \qquad (9.10)$$

If the error is small it is allowed to approach

$$E / (100 + E) \longrightarrow E / 100$$

and

$$E / (100 - E) \longrightarrow E / 100$$

In that case equations (9.9) and (9.10) result in the same equation by which n can be calculated:

$$sqrt\ n = \frac{s * t}{[E / 100] * x(av)} \qquad (9.11)$$

An example on this is given.
The data used are: n(past)=12, x(av)=1.04 ppm and s=0.94 ppm. and are assumed to be data from a sample that is taken before. When a new sample with size n(new)=12 is taken, the chance is 95 % that the new sample mean lies between R1 and R2.

$$R1 = mu(0) - [t(1/2alpha),(n-1)] * s/sqrt(n) =$$
$$= 1.04 - 2.201 * 0.94/sqrt(12) = 1.04 - 0.60 = 0.44 \text{ ppm}$$
$$R2 = mu(0) - [t(1/2alpha),(n-1)] * s/sqrt(n) =$$
$$= 1.04 + 2.201 * 0.94/sqrt(12) = 1.04 + 0.60 = 1.64 \text{ ppm}$$

The expected sample mean varies between $0.44 < x(av) < 1.64$ ppm. The prediction limits differ widely so this is not very valuable.

When a new sample is taken with size n(new)=12, the chance is p % that the average of this sample exceeds R2. Predicted upper limits of the sample-mean arecalculated for some cases in table 26. This table also shows the upper limit value R2 when a new sample with sample-size 1 is taken, with the same probabilities of exceeding this value.

Table 26.

Predicted upper limits of the sample-mean

p	t	R2 n(new)=12	R2 n(new)=1
%	[-]	ppm	ppm
40	0.260	1.11	1.29
25	0.697	1.23	1.69
10	1.363	1.41	2.32
5	1.796	1.53	2.72
2.5	2.201	1.64	3.11

p=probability of larger value (one tailed test)

The conclusion from table 26 can be:

If a new sample with size 1 is taken, the chance is 95 % that this value lies between 0 and 3.11 ppm. This is not very valuable in terms of prediction. In this type of conclusion the magnitude as well as the confidence interval can be varied. Table 27 gives some examples.
In the next section the results of calculations of predicted limit values of sample means are presented dependent on (1) the size of the sample and (2) the confidence interval of the prediction.

8.4 PRACTICAL APPLICATIONS

Approaches A and B from the preceeding section are used here, resulting in ranges of predicted averages of the new sample x(av):

(1) The predicted range of x(av) is calculated from the smallest possible sample size: n(new) = 1 and a variable confidence interval: CI = 95 %, 80 % and 50 % resp.
(2) The predicted range of x(av) is calculated from a maximum ratio of 2 between the upper and lower value of the predicted range. It may be clear that more combinations of CI and n(new) satisfy this ratio: a high CI requires a certain n(new) and a lower CI requires a lower n(new).

In the tables 28 and 29 Results of calculation A are summarized for n(new)=1 and CI=95 %, 80 % and 50 % respectively.

Table 27.

Prediction of sample-means of new samples with varying sizes

sample-size of new samples n(new)	confidence interval [%]	prediction of the sample-mean [ppm]		
1	95	0	< x	< 3.11
2	95	0	< x(av)	< 2.50
4	95	0.01	< x(av)	< 2.07
1	80	0	< x	< 2.32
2	80	0.13	< x(av)	< 1.94
4	80	0.64	< x(av)	< 1.68
1	50	0.38	< x(av)	< 1.69
2	50	0.58	< x(av)	< 1.50
4	50	0.71	< x(av)	< 1.37

How to use the tables will be explained with an example on table 28. If a new sample with size n(new)=1 is taken from the toplayer of lake Westeinder sediments the predicted aluminum-content lies between 0 and 3.156 % dry weight. The confidence interval of this prediction is 95 %. A drop of the confidence interval to 80 % and 50 % reduces the expected range to 0.244 %-2.458 % and 0.782 %-1.920 % resp.

Next the results of calculation method B are presented. Tables 30 and 31 show limit values of the predicted sample means when new samples are taken with sample size unequal to 1. The required n(new) and the predicted limits of the sample mean are now dependent on the expected variance of the elements. This variance is represented by the standard deviation of the data of this study.

Table 28.

Predicted sample-means of new samples in lake Westeinder

The limits R1 and R2 [% of dry weight] are calculated for n(new)=1 and confidence intervals (CI) of 95, 80 and 50 %

CI	95 %		80 %		50 %	
	R 1	R 2	R 1	R 2	R 1	R 2
toplayer in lake Westeinder sediments (0-1 cm)						
Al	0	3.156	0.244	2.458	0.782	1.920
As	0	0.009	0	0.007	0.001	0.005
Ca	3.799	25.421	7.831	21.389	-	-
Co	0	0.006	0	0.005	0.001	0.003
Cr	0.022	0.030	0.023	0.029	-	-
Cu	0	0.081	0.004	0.064	-	-
Fe	0.255	4.403	1.028	3.630	1.660	2.998
K	0.691	1.601	0.861	1.431	-	-
Mg	0	0.279	0	0.192	0	0.120
Mn	0	0.445	0.027	0.349	0.105	0.271
Ni	0	0.004	0.001	0.003	0.001	0.003
P	0.018	0.234	0.058	0.194	0.091	0.161
Pb	0	0.021	0	0.015	0	0.010
Si	11.638	38.322	16.614	33.346	-	-
Sr	0.024	0.076	0.034	0.067	-	-
Ti	0	0.141	0.005	0.109	0.030	0.084
Zn	0	0.064	0	0.047	0.002	0.032
oPw	0	2.706	0.376	2.176	0.812	1.740
tPw	0	5.646	0.129	4.381	1.161	3.349
deep layer in lake Westeinder sediments (45-50 cm)						
Al	0	2.381	0.749	1.749	0.126	1.230
As	0	0.009	0	0.007	0.001	0.005
Ca	0.709	16.061	3.555	13.215	-	-
Co	0	0.006	0	0.005	0.001	0.003
Cr	0.003	0.037	0.009	0.031	-	-
Cu	0.003	0.011	0.004	0.010	0.006	0.008
Fe	0.172	4.340	0.945	3.567	1.580	2.932
K	0	2.411	0.151	1.897	0.574	1.474
Mg	0	0.285	0	0.217	0.043	0.161
Mn	0.023	0.423	0.097	0.349	0.158	0.288
Ni	0	0.003	0	0.002	0.0	0.002
P	0.009	0.099	0.026	0.082	0.039	0.069
Pb	0	0.026	0.002	0.020	0.006	0.016
Si	3.586	34.818	9.375	29.029	-	-
Sr	0.018	0.070	0.028	0.060	-	-
Ti	0	0.174	0	0.128	0.010	0.090
Zn	0	0.043	0.001	0.033	0.009	0.025
oPw	0	3.655	0.100	2.846	0.765	2.181
tPw	0	8.970	0	6.631	0.617	4.707

Table 29.

Predicted sample-means of new samples in lake Elfhoeven

The limits R1 and R2 [% of dry weight] are calculated for n(new)=1 and confidence intervals (CI) of 95, 80 and 50 %

CI	95 %		80 %		50 %	
	R 1	R 2	R 1	R 2	R 1	R 2
toplayer in lake Elfhoeven sediments (0-1 cm)						
Al	0.236	4.874	1.127	3.983	1.826	3.284
As	0	0.014	0	0.010	0	0.007
Ca	7.003	9.869	7.554	9.318	-	-
Co	0.001	0.009	0.002	0.008	0.004	0.006
Cr	0.026	0.034	0.027	0.033	-	-
Cu	0.003	0.035	0.009	0.029	0.014	0.024
Fe	2.643	4.407	2.982	4.068	-	-
K	1.189	1.719	1.291	1.617	-	-
Mg	0	0.608	0	0.443	0.043	0.313
Mn	0.019	0.157	0.045	0.131	0.066	0.110
Ni	0.001	0.005	0.002	0.004	0.002	0.004
P	0.076	0.168	0.094	0.150	-	-
Pb	0	0.044	0	0.030	0	0.019
Si	22.466	32.510	24.400	30.580	-	-
Sr	0.038	0.046	0.039	0.045	-	-
Ti	0.091	0.207	0.113	0.185	-	-
Zn	0	0.018	0	0.013	0.001	0.009
oPw	0	1.179	0	0.872	0.109	0.627
tPw	0	3.148	0	2.361	0.429	1.737
deep layer in lake Elfhoeven sediments (45-50 cm)						
Al	0	3.781	0.701	3.057	1.277	2.481
As	0	0.010	0	0.007	0.001	0.005
Ca	3.487	10.209	4.767	8.929	-	-
Co	0	0.008	0.001	0.007	-	-
Cr	0.022	0.030	0.023	0.029	-	-
Cu	0.004	0.012	0.005	0.011	-	-
Fe	1.242	5.398	2.033	4.607	2.662	3.978
K	0.160	2.748	0.653	2.255	1.044	1.864
Mg	0	0.438	0.078	0.354	0.146	0.286
Mn	0.047	0.161	0.069	0.139	0.086	0.122
Ni	0.001	0.005	0.002	0.004	0.002	0.004
P	0.027	0.123	0.045	0.105	-	-
Pb	0	0.043	0.004	0.034	0.011	0.027
Si	8.616	35.020	13.643	29.993	-	-
Sr	0.023	0.067	0.031	0.059	-	-
Ti	0.024	0.186	0.055	0.155	-	-
Zn	0	0.044	0.005	0.035	0.012	0.028
oPw	0	1.623	0	1.241	0.301	0.937
tPw	0	2.176	0.212	1.714	0.579	1.347

Table 30.

Predicted limits of sample-means of new samples, lake Westeinder

The new sample has size n and is calculated for two layers: 0-1 and 45-50 cm. Confidence interval of the prediction is CI %. Boundary condition of the calculation is a ratio of 2 between upper (R2) and lower limit (R1) of the sample mean.

layer	0 - 1 cm				45 - 50 cm			
	n	CI	R1	R2	n	CI	R1	R2
		[%]	[% of dry weight]			[%]	[% of dry weight]	
Al	6	80	0.899	1.803				
	2	50	0.949	1.753	6	50	0.453	0.903
As	4	50	0.002	0.004	4	50	0.002	0.004
Ca	5	95	9.775	19.445	8	95	5.671	11.099
	2	80	9.817	19.403	3	80	5.596	11.174
Co	4	50	0.0013	0.0026	4	50	0.0013	0.0027
Cr	1	95	0.022	0.030	7	95	0.014	0.026
					3	80	0.014	0.026
Cu					4	95	0.005	0.009
	7	80	0.023	0.045	2	80	0.005	0.009
Fe	7	95	1.545	3.113	8	95	1.519	2.993
	3	80	1.578	3.080	3	80	1.500	3.013
	1	50	1.660	2.998	1	50	1.580	2.932
K	2	95	0.824	1.468	7	80	0.694	1.354
					2	50	0.706	1.342
Mg	20	50	0.038	0.052	3	50	0.068	0.136
Mn					8	95	0.152	0.294
	7	80	0.127	0.249	3	80	0.150	0.296
	2	50	0.129	0.247	1	50	0.158	0.288
Ni	10	95	0.0013	0.0026				
	4	80	0.0013	0.0027				
	1	50	0.0013	0.0027	4	50	0.0007	0.0013
P	7	95	0.085	0.167	7	95	0.037	0.071
	3	80	0.087	0.165	3	80	0.038	0.070
	1	50	0.091	0.161	1	50	0.039	0.069
Pb					7	80	0.007	0.015
	17	50	0.003	0.005	2	50	0.008	0.014
Si	3	95	17.277	32.683	6	95	12.827	25.577
	1	80	16.614	33.346	3	80	13.528	24.876
Sr	3	95	0.035	0.065	3	95	0.029	0.059
	1	80	0.034	0.066	1	80	0.030	0.060
Ti	8	80	0.038	0.076				
	2	50	0.038	0.076	6	50	0.034	0.066
Zn					8	80	0.011	0.023
	7	50	0.011	0.023	1	50	0.011	0.023

Table 30 continued

Interstitial water								
	n	CI	R1	R2	n	CI	R1	R2
		[%]	[ppm P]	[ppm P]		[%]	[ppm P]	[ppm P]
oPw	9	95	0.799	1.753				
	5	80	0.874	1.678	8	80	0.988	1.958
	1	50	0.812	1.740	2	50	0.973	1.973
tPw	8	80	1.503	3.007				
	2	50	1.481	3.029	6	50	1.827	3.497

Table 31.

Predicted limits of sample-means of new samples, lake Elfhoeven

The new sample has size n and is calculated for two layers: 0-1 and 45-50 cm. Confidence interval of the prediction is CI %. Boundary condition of the calculation is a ratio of 2 between upper (R2) and lower limit (R1) of the sample mean.

layer		0 - 1 cm				45 - 50 cm		
	n	CI	R1	R2	n	CI	R1	R2
		[%]	[% of dry weight]			[%]	[% of dry weight]	
Al					10	95	1.278	2.480
	3	80	1.730	3.380	4	80	1.290	2.468
	1	50	1.826	3.284	1	50	1.277	2.481
As					8	80	0.002	0.004
	6	50	0.002	0.004	2	50	0.002	0.004
Ca	1	95	7.003	9.869	3	95	4.908	8.788
					1	50	4.767	8.929
Co	7	95	0.003	0.007	8	95	0.003	0.005
	4	80	0.004	0.006	3	80	0.003	0.006
	1	50	0.004	0.006	1	50	0.003	0.005
Cr	1	95	0.025	0.034	2	99	0.020	0.032
Cu	6	95	0.013	0.025	2	95	0.005	0.011
	3	80	0.013	0.025	1	80	0.005	0.011
Fe	1	95	2.643	4.407	4	95	2.281	4.359
					2	80	2.410	4.230
K	1	95	1.189	1.719	7	95	0.965	1.943
					3	80	0.991	1.917
Mg					10	95	0.146	0.286
					4	80	0.147	0.285
	5	50	0.118	0.238	1	50	0.146	0.286
Mn	6	95	0.060	0.116	3	95	0.071	0.137
	2	80	0.058	0.118	1	80	0.069	0.139
	1	50	0.066	0.110				
Ni	3	95	0.002	0.004	3	95	0.002	0.004
	2	80	0.002	0.004				
P	2	95	0.090	0.154	4	95	0.051	0.099
					2	80	0.054	0.096
Pb					6	80	0.013	0.025
	11	50	0.005	0.011	2	50	0.014	0.024
Si	1	95	22.466	32.510	4	95	15.217	28.419
					2	80	16.037	27.599
Sr	1	95	0.038	0.046	2	95	0.029	0.061
					1	80	0.031	0.059
Ti	2	95	0.108	0.190	6	95	0.072	0.138
	1	80	0.113	0.185	3	80	0.076	0.134
Zn					5	80	0.013	0.027
	7	50	0.003	0.006	1	50	0.015	0.025

Table 31 continued

Interstitial water								
	n	CI	R1	R2	n	CI	R1	R2
		[%]	[ppm P]	[ppm P]		[%]	[ppm P]	[ppm P]
oPw					9	80	0.412	0.826
	5	50	0.252	0.484	3	50	0.435	0.803
tPw					5	80	0.627	1.300
	4	50	0.756	1.410	2	50	0.691	1.235

From this table it is clear that a prediction with a smaller confidence interval results in a smaller required sample size and a smaller range between the upper and lower limit value of the sample mean.

8.5 CONCLUSIONS ON SOME ELEMENTS

Conclusions from the preceeding tables on some elements are:

Arsenic
On both depths (0 to 1 cm and 45 to 50 cm) in the lake Westeinder sediments the sample size should exceed 10 samples if predictions are made with a confidence interval of 80 % or larger (with R2 = 2 * R1). In lake Elfhoeven sediments a prediction with confidence interval of 80 % can only be done in the deep layer resulting in a n(new) = 8 (table 31).

Copper
A new sample with size 1 results in widely varying limit values of copper in Westeinder sediments on both depths and in Elfhoeven sediments in the toplayer. Tables 30 and 31 show that predictions with a confidence interval of 95 % require samples with a size of > 10 and 4 resp. in Westeinder sediments and of 6 and 2 in Elfhoeven sediments in toplayer and

deep layer resp. Dropping the predicted confidence to 80 % these sample sizes become 7, 2, 3 and 1 resp.

Iron

The iron-content in lake Westeinder is more varying than in lake Elfhoeven sediments. This is reflected in the predicted iron-values when n(new) = 1. In the Westeinder toplayer and deep layer these contents vary from 0.26 - 4.4 % Fe and from 0.17 - 4.34 % Fe for a confidence interval of 95 %. A prediction with a confidence interval of 95 % and an accepted factor of 2 as range af the predicted averages thus results in a sample size for lake Westeinder of 7 (toplayer) and 8 (deep layer) and for lake Elfhoeven of 1 (toplayer) and 4 (deep layer) for the new sample. n(new) $\leq$ 10.
for the deep layer n(new) = 4 (50 %). A larger

Phosphorus

The expected phosphorus contents when n(new)=1 and the confidence interval is 95 % are for lake Westeinder sediments 0.018-0.234 % P (toplayer) and 0.009-0.099 % P (deep layer). In lake Elfhoeven sediments these are 0.076-0.168 % and 0.027-0.123 % P resp. This results in predictions with limit values within a range of 2 of the sample size for lake Westeinder of n(new)=7 (95 %) for both toplayer and deep layer and for lake Elfhoeven of n(new)=2 (95 %, toplayer) and n(new)=4 (95 %, deep layer). These sample sizes are acceptable. Dropping the confidence interval of the prediction to 80 % these sample sizes become 3, 3, 1 and 2 resp. When a smaller range between the upper and lower limit value is required, these sample-sizes will of coarse increase. $\leq$ 10 if done within the 50 % confidence interval.
The limit

o-PO4 in the interstitial water

The ortho-phosphate concentrations of the interstitial water of the sediment of the two lakes is very variable on both depths. The expected contents vary strongly when n(new) = 1, in spite of the confidence interval which is chosen. A confidence interval of 80 % results in a required sample size of 5 and 8 (lake Westeinder) and > 10 and 9 (lake Elfhoeven) in the toplayer and the deep layer resp. Reduction to 1, 2, 5 and 3 samples is possible, resulting in a prediction with a confidence interval of 50 %. For ortho-phosphate, highly important in eutrophication problems, it is advisable to stick to a somewhat higher confidence interval of prediction and thus in a larger sample size.

t-P in the interstitial water

The total phosphate concentrations of the interstitial water of both lake sediments also belong to the parameters that vary considerably. The variation is somewhat less than with the ortho-phosphate concentration in lake Elfhoeven but somewhat larger in lake Westeinder interstitial waters (both depths). Predictions of average values within a range of a factor 2 of a new sample (80 % confidence interval) results in required sample sizes of 8 and > 10 for lake Westeinder sediments (toplayer and deep layer) and > 10 and 5 samples resp. for lake Elfhoeven sediments.

Lowering the confidence interval of the prediction to 50 % results in sample sizes of 2, 6, 4 and 2 resp.

It can be concluded that the maximum efficiency of a sampling program can be obtained when the program is executed in two steps. The first step gives an impression of the composition of the lakebed and the distribution of the contents in the sediment. From the results in this first step, some types of conclusions can be drawn. the elements that are fairly uniform spreaded over the lake and in the sediments do not need additional information. About the elements that vary strongly, an additional, second step program, needs to be executed. The size of the additional sampling program can be calculated from the results, achieved in the first step of the sampling program.

8.6 TEST OF THE PREDICTED SAMPLE-MEANS

In order to check the statistiocal predictions that were made in the preceeding tables, samples were taken from 9 dutch lakes and at two depths (0-1 cm) and (45-50 cm). Results are summarized in table 32.
When these results are compared to the predictions it appears that in nearly all cases, the predictions proved to be correct. Only in two cases in the toplayer of Westeinder sediments, marked with a * in table 27, the observed sample-mean was smaller than the calculated mean.

8.7 STATISTICAL ASPECTS: SAMPLING STRATEGY VERSUS FIXED NORMS

In this section the measured concentrations in lake Westeinder and lake Elfhoeven are discussed in relation to the legislation and other methods for judgement of soils. Knowledge of environmental hazards of sediments is largely missing. In general sampling must meet norms. Norms however do not meet aspects of sampling. Some qualitative discussion on this is given here.

In order to protect the environment, several governmental regulations came into force. One of them is the Chemical Substances Bill, a law concerning chemical waste and oil products. The enforcements of the law require permits for storage, transport, handling and destruction of a large number of elements and compounds divided in four groups with increasing allowable concentration: groups A (50 ppm allowed), B (5000 ppm), C(20000 ppm) and D(50000 ppm tolerated). The concentrations measured in this study are, with a few exeptions, all below the relevant levels. The exeptions will shortly be dealt with below.

Next to the Chemical Sustances Bill the Soil Clean-up (interim) Act distinguishes three categories of pollution of soils and sludges:

A: representing a non polluted reference value

Table 32.

Results of phosphate analyses of new samples

The lakes are mentioned on maps in chapter II, sampling was done on different days

Lake	P(sed,av)	s of sample	s of mean	n
	% of dry weight	% of dry weight	% of dry weight	sample size
Layer 0 - 1 cm				
Elfhoeven	0.096	0.009	0.032	13
Elfhoeven	0.095	0.005	0.018	13
Elfhoeven	0.097	0.005	0.018	13
Groot Vogelenzang	0.133	0.025	0.044	3
's Gravenbroek	0.124	0.007	0.017	6
's Gravenbroek	0.095	0.014	0.027	4
Kalverbroek	0.102	0.008	0.023	9
Klein Elfhoeven	0.123	0.006	0.011	3
Klein Elfhoeven	0.142	0.010	0.029	9
Klein Elfhoeven	0.145	0.009	0.015	3
Nieuwenbroek	0.092	0.009	0.026	8
Ravensberg	0.124	0.007	0.016	6
Vrijhoef	0.124	0.006	0.015	6
Vrijhoef	0.122	0.005	0.010	4
Westeinder	0.090	0.009	0.045	24
Westeinder	0.050	0.007	0.028	16*
Westeinder	0.064	0.009	0.032	14*
Layer 45 - 50 cm				
Elfhoeven	0.057	0.009	0.030	11
Elfhoeven	0.095	0.003	0.009	7
Klein Elfhoeven	0.058	0.012	0.020	3
Westeinder	0.066	0.007	0.033	24
Westeinder	0.046	0.005	0.019	16
Westeinder	0.045	0.005	0.019	15

B: test criterium for soil inquiry
C: test criterium for a so called further inquiry or for direct action to put the soil on a sound basis again

The metal concentrations in soils and sludges belonging to these three categories are listed in a guideline for soil clean-up used by the Department of the Environment. These values are used next to the guidelines given by the European Community and WHO that also provide limit values for several substances in water. Often no direct toxicity of these substances is known. General and specific resist play an important role in the effect of substances to man but the dose makes the substance toxic. Some people state that only after scientific evidence, substances can be called toxic and than only in relation to the dose. It is true that knowledge about the effect of specific (heavy) metals (eg cadmium, magnesium and zinc) on specific locations of for instance amino-acids on cellular level is missing. Knowledge is also missing about specific positive functions, if there are any, of lots of these compounds, especially to man. It may be wise however, not to give the benefit of the doubt to those substances under suspicion. It could take several years before scientific evidence about effects can be given. Meanwhile it seems to be better to prepare and carry out measurements, aimed at push back of use and discharge of elements and compounds which are already under suspicion. Moreover, if discharged, these compounds are very hard to eliminate from the environment and at high costs, as appeared in the recent past.

With a few exeptions, the contents of the elements of both lakes are all below the threshold values per group of compounds mentioned in the directions for the enforcement of the Chemical Substances Bill (1977 and 1979). Only the maximum values of arsenic, calcium and chromium (average and maximum values) are higher than indicated in the law. Although the other elements do not exceed the threshold values of the directions for the enforcement of the law, their possible toxic influence should of course not be neglected. Compared to the soil clean-up act several data exceeded A, B and C standards.

<u>Arsenic</u> Compared to the directions for the enforcement of the Chemical Substances Bill, the average As-content in both lakes are below the maximum tolerable limits of 50 ppm (Class A element). On some locations however in both Westeinder and Elfhoeven sediments this 50 ppm limit is exceeded.
Maximum values of 140 ppm (lake Westeinder) and 130 ppm (lake Elfhoeven) were measured. In this respect the sediment should locally be considered as chemical waste. In the law, arsenic as well as arsenic compounds are mentioned in class A so the measured concentrations are decisive. The A, B and C standards of the soil clean-up act are again exceeded on several locations.

<u>Chromium</u> Chromium is mentioned as one of the elements in the Chemical Substances Bill (1979). Two ions of this element are mentioned, which have different properties with respect to toxicity, bioaccumulation and persistence. Cr(III) compounds are considered to belong in class B which allows maximum concentrations of 5000 ppm (0.5 % by weight). Cr(VI) compounds however are considered to belong in class A (the highest toxicity etc.) and maximum concentrations of only 50 ppm (0.005 %) are allowed. No distiction could be made between the two ions in this study, due to the bulk-type of the XRF-analysis. It is therefore not clear wheather or not sediment is to be considered as chemical waste as far as Chromium is concerned. Application of analysis techniques with which the two ions can be determined separately should therefore be considered. Special care will be necessary in that case in order to prevent changes in the oxidation status of the sediment in the time between

sampling and analysis. Here the soil clean-up act was exceeded several times. This is illustrated below.

In relation to the categories A,B and C *an inquiry should be* instituted for

(1) the average values of arsenic, copper, chromium and lead
(2) the maximum values of arsenic, chromium, cobalt, copper, lead, nickel and zinc.

A further inquiry followed by measurements would be necessary with respect to the maximum values of arsenic, chromium, cobalt, *lead, nickel and zinc.*

According to the legislation the sediments partly consist of chemical waste. It is however a natural sediment in which the concentrations show some local peaks and the average concentration lies below the level mentioned in the legislation. Here, it is clear that statistics and legislation have *different points of view from* which they look at measured concentrations. A good example is calcium.

Calcium Application of the list of elements and compounds in the According to the Chemical Substances Bill calcium is a group D element with a *tolerated concentration of 50000 ppm* (5 % dry weight). Compared to this upper allowed limit value *very few* measured concentrations are tolerable. However, it can be expected that most of the calcium is bound as Ca-carbonates and Ca-phosphates, both not considered to be chemical waste. This will probably also be the case with natural calcareous components of the sediments. They are not mentioned in the list of *exeptions in the directions of the* enforcement of the law, however. It can therefore be asked what the meaning is behind the legislation with respect to calcium. The poverty of standards and criteria is also indicated by Vonk (1982) and van Gemert (1982).

Statistical defined standards

Standards for soils and sediments are more difficult than those for water because of heterogeneity of soils. The standards in the legislation are stated in absolute and not in stochastic terms. The observed concentrations in the aquatic sediments do differ largely, as was clearly shown in the preceeding chapters. It therefore is considered that the *given standards* should be statistically defined. When local accumulations of an element are observed, as is the case in lake Westeinder and Elfhoeven sediments mostly on random locations, these individual observations do not necessarily represent the lakebed. It is one observation from a distribution of concentrations in the lakebed.

Suppose a fixed standard for a given element as concentration S. The element has a standard normal distribution in the lakesediment around the mean X with a standard deviation of sd. When the standard deviation is zero, any sample can be classified as right (X<S) or wrong (X>S). When the noise *of the element is large, a fixed standard will* result in many unjust 'wrongs', when the average concentration still is X. When the standard is lowered to [S - 2*sd], the chance of exceeding the standard is 2.5 %. The tolerated standard

deviation around the standard should be dependent on the lake under investigation, because of the large observed noise in measured concentrations. The standard can thus be considered together with the standard deviations of the observations.

This can be illustrated with an example
For arsenic the standard deviation was about equal to the sample mean. This means that the standard can be changed to [S(As) ± sd(As)] = [S(As) ± S(As)].
Suppose the standard is 10 units. When one sample is taken and the concentration is 8 units, that sample can be judged right.

With the knowledge we obtained about spatial vatiation a possibly better approach is given below.
The noise in the measurements will probably be considerable. *An example: the characteristics of 9 samples are:* average is 8 ± 4 units, which means that a large part of the total sediment area should be considered wrong. Must this be accepted or not. If not, the solution lies in an adapted standard. If the standard is 10 ± 5, the sample with distribution of *8* ± 4 can comply the standard with a desired level of accuracy. Without this statistical approach the standard is not operative for elements with a *large noise in the observations* like in our case arsenic. In fact possible synergistic and antagonistic effects should be included in a standard, that then contains the risk assessment of all elements involved.

When a statistical standard is accepted, more samples have to be taken than in most cases is done *now. The cost* is higher but a more precise picture of the situation is obtained.

An important difficulty that arises when statistical standards *are adopted, is which* discharge of effluent is responsible for exceeding the standard. The last discharge fills up the tolerated concentration but is possibly a small *one.* When the discharges and the risks of each discharge can separately be judged, the best decision can be taken on stopping or reducing discharges.

Chapter IX

NEW EQUIPMENT FOR UNDISTURBED SEDIMENT SAMPLING

9.1 INTRODUCTION

This work aimed at the recognition of structures, both horizontally as vertically, in lake sediments. For this type of research data must be collected from several thin layers in the upper part of the sediments. To trace existing structures in the toplayers of the sediments, it is essential that the samples are undisturbed (Siebers and Donze, 1984 and Siebers, 1982). When samples are taken from lake- and riversediments, disturbances of the sample often occur. This is the case with the majority of the existing sampling equipment. Even the equipment that we used in this study did not provide undisturbed sediment cores under all circumstances. We had to discard several disturbed or unreliable sediment cores, before we had obtained the 30 undisturbed cores, that we used for this study. Far more time and money than desired is thus involved in the sampling procedure, as a consequence. To solve this problem, we considered to develop sampling equipment with which undisturbed cores from almost any type of sediments underlying rivers and lakes can be obtained. Development of equipment that suits this demand requires an integrated solution for technical problems as operation, construction, closing mechanisms and for economical problems as costs and marketability.

The results as discussed in this chapter were achieved in a project, that was subsidized by the Ministry of Economic Affairs of the Dutch Government (Siebers, 1983). The projectgroup consisted of Prof. Dr. M. Donze and the author of this thesis, at that time both researchers of the Delft University of Technology, Eijkelkamp Equipment for Soil Research BV, Giesbeek, the Netherlands and L. Teerling, adviser for innovation projects.
Mr J.J. Gerritsen (KEMA NV, Arnhem) rendered valuable assistance during development and testing.

9.2 DEVELOPMENT OF NEW EQUIPMENT

Several researchers did put energy in the development of new or in the adaption of existing equipment (a.o. Mortimer, 1941, Ambuehl, 1969, Murray, 1976, Niemisto, 1974). In most cases they stopped development work at a moment that the sampling procedure had become reliable enough and gave enough information for research needs. Existing equipment is in most cases bought or developed in relation to a specific research project, often dealing with a fairly homogeneous sediment type. When the same equipment is applied for other types of sediment it is often not functioning well. The simple fact that each sub-water soil is different leads to difficulties in the work. The sampling conditions on different locations within each *lake or river area can vary* strongly. Irregularities in the level of the bottom can easily cause deviations from the vertical when the equipment penetrates the sediment. This leads to a limited employment of the equipment: only in restricted situations a good sample is obtained. We therefore considered the demands for sampling equipment, that supplies a reliable sample of de*sired size, succesful any time and under all circumstances.* We decided that the equipment must be fitted with interchangeable accessories. This led us to the idea to construct a main frame with different accessories. Several sets of equipment can be composed now from these modules, each entirely suitable for the expected different field situations.

9.2.1 Starting points and equipment demands

The best possible equipment is defined:

'Ideal' corer-equipment is:

an independant corer, loosely connected to the boat. The corer is able to descend through the water slowly and independently, and lands gently on the sediment to be sampled. After this the apparatus adjusts itself vertically and is able to penetrate the sediment till the required depth. The corer removes itself from the sediment, returns to the water surface, still in vertical position and can be recovered by the ship. Almost any type of sediment can be sampled this way.

As it is not realistic -and practically not possible- to combine all these options in a first prototype, minimum demands for coring equipment are also defined. We decided to first develop the equipment that suits the minimum demands and to a step by step improvement and extension to the ideal corer. Future developments can include instrument addition to the corer for measurements of waterdepth, pH, redox, tur*bidity and conductivity, but also a pore-water sampler can* be attached to the frame.

A 'minimum' corer is:

a corer, descending through the water connected tightly to the boat by a cable or bar. The equipment is able to land fairly gentle and is kept about vertically by a framework. The degree of verticality is dependent on the degree of the flatness of the underwatersurface. Next the corer must be driven into the sediment from the anchored ship. After this, the sampling tube with the sediment core in it, is closed at the upper end and, if necessary, also at the lower end. Then the equipment is withdrawn from the sediment, pulled up in vertical position and recovered. In principle, it must be possible to sample any type of sediment.

From the definitions, criteria for design were arranged (table 33).

Table 33.

Criteria for sediment sampling equipment

Apparatus *dimensions* and construction	- diameter and length of the sample - *materials* - weight
Sampling Procedure	- maximum waterdepth to be used in - degree of independency .connection to ship loose or tight - gentle landing on top of the *sediment* .independently to required, adjusted depth .independently by gravity .hammering pneumatically, vibration .hammering by handpower - vertical penetration - closing the sampling tube .upper end: vacuum, rubber ball, inside valves, piston, none .lower end: ball valve, inflatable rubber, diaphragma, wire-spring, foam, freezing, rapidly hardening concrete, outside valves, none - withdrawal from sediment .independently on command .pull with winding gear, balloon, manpower
Operation	- can the apparatus easily be operated - can the sampling tube easyly be removed, and changed for a new one
Result	- degree of (un)disturbance - removing the sampling tube - necessary manipulations with the sample in the tube
Availability	- availability, price, patents

Existing sampling equipment is compared to the criteria men*tioned in table 33. All equipment is fitted with a single,* mostly fixed cutting head or cutting edge. This can result in field situations that no sediment sample of the chosen length can be taken on the chosen location, for instance because the equipment cannot be forced to penetrate to the desired depth into the sediment. The concept of a sediment sampler should in fact aim at a unit that can be fitted with several cutting heads, that can be assembled to the basic apparatus in case it is required by the type of sediment encountered.

9.2.2 Description of the sampling equipment

The best possible sampling procedure is:

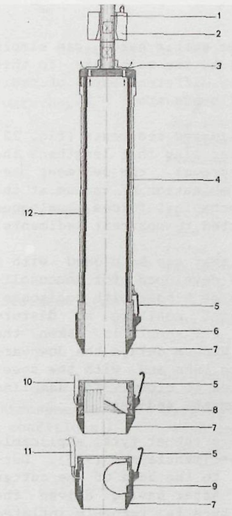
(1) execute the sampling with the most simple construction. When a good sample is obtained the procedure is finished.
(2) when the sampling failed, the obtained knowledge about the sediment type leads to the best possible assembly of the equipment
(3) carry out the sampling procedure with the assembled combination

We decided to construct a prototype of the new equipment, that exists of a stainless steel main tube frame, containing *an inter-changeable perspex sampling tube.* At the upper end a vacuum closing device is incorporated, the inter-changeable closing mechanisms at the lower end of the tube are remote controlled. We did not use scuba divers like Evans and Lasenby (1984). Some strict requirements were made on the new equipment:

(1) *the sediment sample must always be undisturbed*
(2) it must be possible to take samples from 'any' type of sediment under all reasonable circumstances
(3) the construction must be such that the length of the sediment core can freely be chosen, less or equal to the maximum length of the perspex sampling tube
(4) penetration into the sediment must be possible from the boat, so *at a distance*
(5) No deviations of the vertical are allowed when the equipment penetrates the sediment.
(6) removal of the sampling-tube on board of the ship must be possible (a) without disturbing the sediment sample, (b) without losses of sediment and (c) easy, fast and reliable
(7) *it must be possible to transport and treat every sediment sample separately*
(8) the equipment must be built up from separate modules
(9) the equipment should be salable beginning with the most simple version extendable with all accessories separately

The remote controlled penetration was made possible by connection bars between the equipment and the ship (figure 22, no 1). The number of connection bars is adapted to the water depth. The connection bars also serve as pulling device for withdrawal.

The sampling equipment is constructed from a stainless steel main frame (figure 22, 12), in which the perspex sampling tube (4) is pinched between the vacuum closing device and the cutter head (6/7).
At the top end a rubber membrane (fig 22, 3) allows an undisturbed air-release and outflow of water during descend. When the sample is taken and the equipment is withdrawn from the sediment, the rubber membrane causes vacuum. The membrane, guarded with a weight (2), also prevents water from disturbing the sample during upward movement of the equip*ment through the water.*



1	connection bars
2	weight
3	membrane for vacuum closing
4	*perspex sampling tube* 120-110 mm outer and inner diameter
5	connection clamps
6/7	open cutter head with cutter edge
8/7	cutter head with *lamellae*
9/7	cutter head with rubber tyre; inflatable
10	steel cable
11	tube to inflate rubber tyre
12	stainless steel main *frame*

Figure 22: Cross-section of the new sediment sampling equipment

The sampling apparatus is connected to the boat by a number of interconnected steel bars. The number of bars is adapted to the waterdepth. The apparatus is hammered into the sediment by hand. A standard hammering device can be screwed on top of the upper bar. A life-line is connected to the equipment. The steel bars also secure the position of the boat.

Withdrawal from the sediment is easy when a special pulling device is fixed to the connection bars (pulling) and glides along them (for repacking) alternately. In order to remove the sampling tube from the mainframe easily, rapidly and reliable, we designed a frame in which the equipment is hanged in upright position on supports. Next all connection bars and weights can be removed and the sample can be removed *from the mainframe.*

For sampling programs, where the demands are less severe, a smaller type of equipment is developed. The diameter is about 0.07 m and the maximum sample length about 60 cm. This equipment has one cutter head (inflatable tyre) that can easylily be replaced in case of disruption. Both instruments *form part of the tender of delivery of* Eijkelkamp Equipment for Soil Research BV, Giesbeek, the Netherlands. The sample length is shorter than e.g. Zuellig (1956) but suits in most cases and can be constructed longer.

9.2.3 Closing mechanisms

At the lower end, inter-changeable cutter heads can simply be attached by *clamps (fig. 22, 5) to the mainframe. In this* way the equipment can be adapted to different types of sediment encountered. The three cutter heads are:

(1) an open cutter head for consolidated sediments (fig. 22, 6/7). This is in fact a sharp cutter ring that lengthens the stainless steel tube. During withdrawal, the sediment remains in the sampling tube by a *combination of vacuum at the* top-end, cohesion, adhesion and mechanical forces, analogous to a silo. Application is restricted to coherent sediments.

(2) a cutter head with lamellae that can be closed with a cable (fig 22, 8/7). This head is developed for unconsolidated sediments. The lamellae work as hinges with horizontal axis. Fixed magnetically in upright position, no disturbance of the sample occurs. When the sample is taken, the *apparatus is slightly withdrawn.* Vacuum delays the downward movement of the sample through the tube and with the steel cable (10) the lamellae are forced to close. The sampling equipment can now be withdrawn from the sediment.

(3) a cutter head with an inflatable rubber tyre, applicable for unconsolidated and very thin sedimentlayers (9/7). During *sampling, the tyre lies fixed to the edge of the cutter* head (vacuum within the tyre). After having driven the equipment into the sediment, the tyre is remotely inflated (11). The rubber is proof against stones, branches, etc. If very sharp objects like pieces of shells occur frequently in the sediment, the cutter head with lamellae should be used.

With these three inter-changeable cutterheads it is possible to simply adapt the sampling equipment in the field.

9.3 EXPERIENCES IN FIELD SITUATIONS

9.3.1 Tests of the equipment in the field

The prototype is tested several times in different field situations. These are shown in table 34.
The equipment was tested in several fieldsituations with people that were not familiar with the equipment. We thus simulated future buyers, provided with a manual and a one-hour instruction. The expectation of buyers is to have several good, undisturbed cores at the end of the day. Remarks *from the tests resulted in some adaptions of the equipment,* thus improving the design and control. The tests gave good results and were followed by the use of the apparatus in an existing research project together with The Watercompany of the City of the Hague and Dr. A.M. van der Kraan and E. Gerkema, researchers at the Interuniversitary Reactor Institute at Delft. Cores were taken in the Andelse Maas Basin, a connection between the rivers *Rhine and Meuse as described* in chapter VII (de Kruijk et al, 1984). The equipment provided excellent undisturbed cores. The sediment surface was fully intact and no disturbance along the tube occurred.

Table 34.

Testconditions of the new equipment in the field

Waterdepth	- *very shallow, operation: standing in water* - shallow water, operation from a bridge - shallow water, operation from a small boat - running water till 8 m depth, operation from a large boat
Watertype	- ditch - *lake* - river - spreading pond
Sediment type	- peaty sediments - clay-like sediments - sandy sediments - thin toplayers of sediments - sludge drying-beds (water-treatment)
Atmospheric conditions	- varying from nice, calm and sunny to wind and rain

Chapter X

DISTRIBUTION OF 20 ELEMENTS, INCLUDING HEAVY METALS IN THE SEDIMENTS

10.1 INTRODUCTION

The distribution of the concentrations of 20 elements, including heavy metals, in the sediments of lake Westeinder and lake Elfhoeven is discussed and the concentrations are compared to those, measured in other lake- and river-sediments. Literature was obtained with techniques, described in Siebers and de Jong (1983). When variations are observed *this can lead to recognition of patterns.*
Thirty cores were taken from the sediments, 17 from lake Westeinder and 13 from lake Elfhoeven. The cores were sliced (fig. 9) and subsamples of 5 slices, representing five depths in the sediments, were chemically analysed. These depths are: 0-1 cm, 4-6 cm, 8-10 cm, 25-30 cm and 45-50 cm. The concentrations are expressed as percentage of the dry *weight of the sediment. The average concentration and the* standard deviations were calculated for both lakes and for each of the five depths in the sediment. On 16 sediment depths the concentration of phosphate in the sediment and the ortho- and total-phosphate concentration of the interstitial water were determined

Next to the standard deviation mentioned above, the standard deviation of the mean has been calculated. The standard deviation of the sample (s) is a statistical estimation of the range of the individual observations of the sample as taken from the lake-sediments. It thus is an estimator of variation of the population and is the square root of the sample variance:

$$s(sample) = sqrt\,\left[\,\frac{(\,x(i) - \bar{X}\,)**2}{n-1}\,\right]$$

One of the purposes of the investigations was to obtain an estimate of the average of the population. This brings up the question of the accuracy of the samplemean as an estimator of the population mean. If repeated random samples of size n are drawn from any population that has mu as mean and sigma as standard_ deviation, *the frequency distribution of* the samplemeans $\bar{X}$ has mu as mean again and sigma/(sqrt n) as standard deviation (Snedecor and Cochran, 1967). This standard deviation of the mean is also called the standard error.

The samplemean thus is an unbiased estimator of the population mean. The standard error is obtained when the sampling is repeated n times, n is the original samplesize. The relation between the two standard deviations is:

$$s(mean) = \frac{1}{sqrt(n)} * s(sample)$$

Data of the analysis were operated by the SPSS - STATISTICS program (Nie et al, 1975 and Hadlai Hull and Nie, 1981). The SPSS statistics program has an option to test the validity of the assumption of standard normal distribution by calculation of the skewness and the kurtosis parameter. These were all acceptable (Pearson and Harley, 1954).
For every element the average value, the standard deviations of sample and mean as well as minimum and maximum concentration are tabulated for each of the five depths and for the average concentration in a sedimentlayer of 50 cm thickness. The average concentration in the tables in this chapter were calculated as arithmic mean of the measured concentrations on five depths. It is not calculated as weighed mean since the weighing factors can only be estimated. This does not improve accuracy. Large differences between concentrations in subsequent layers that may influence the result are discussed separately. Weighing in horizontal direction was not considered. All original data on the copper and phosphate concentrations are given in this chapter. For the other elements the data are already published (Siebers, 1982). The complete dataset can be ordered separately.

Further, the measured concentrations are compared to concentrations measured in other lake- and river-sediments. This comparison gives an indication on existing concentrations. The measured concentration depends on many variables like hydrology, geology, vegetation, etc. but also on the history of pollution. From the average values per sedimentlayer, depth structures of the elements can be recognized. It appeared however, that in most cases, the depth structure was smaller than the vertical variability of the concentrations in the sediments. For every element some data from other research are presented as illustration on the data found in this study. For some elements, Salomons and Forstner (1984) published base line data. These are given below in table 35.

10.2 ALUMINUM

Contents and comparison

Aluminum contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 36. Some data of lake- and river-sediments from other sources are summarized in table 37.

Table 35.

Background concentrations of heavy metals in sediments and soils

(after Salomons and Forstner, 1984)

metal	shale and clays	sub-recent Rhine sediments	lacustrine sediments	soils
	ppm	ppm	ppm	ppm
Fe (%)	4.72	3.23	4.34	3.2
Mn	600	960	760	760
Zn	95	115	118	59.8
Cr	83 (*60)	47	62	84
Ni	68 (*32)	46	66	33.7
Cu	45 (*31)	51	45	25.8
Pb	20	30	34	29.2
Co	19 (*13)	16	16	12
Hg	0.2	0.2	0.35	0.098
Cd	0.2	0.3	0.40	0.62

* recent freshwater sediments

Discussion

Aluminum, after oxygen and silicon, is the most abundant element in the earth crust. It is found as felspars. In this study total amounts of aluminum were measured. The average aluminum contents in lake Elfhoeven sediments are two- to threefold those of lake Westeinder at all depths in the sediments. This is at variance with the field observation that the sediments of lake Westeinder contained more clay than those in lake Elfhoeven.
The average aluminum contents of the sediments in the utmost toplayer are 20-50 % higher than in all deeper layers of the sediment. The maximum aluminum content is about the same in the two lakes. In lake Westeinder these aluminum peaks occur in two cases in deeper layers, in lake Elfhoeven one single peak is observed in the toplayer.
The observed decrease with depth was also measured by Allan and Brunskill (1976) who observed an increase again in several cores in layers deeper than 50-55 cm. This increase was not observed in our lakes.
In the layer from 4-10 cm the values are more uniformly distributed than in other layers, resulting in considerably lower standard deviations. This was observed in both lakes at this same depth. This can be caused by dispersion mechanisms that influenced the distribution of aluminum in this layer. Whirling up of the toplayer, followed by resettling of well mixed sediment in the recent past and a more uniform occurrence of aluminum in this layer is a possible explanation. It is unknown to what degree the sediment layer is influenced by wind and waves. This will depend on the lakedimensions and -surroundings, the waterdepth, the windforce and the condition of the sediments. If this dispersion occurs, sampling the toplayer just after a storm event should

Table 36.

Aluminum-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Aluminum Westeinder					
0 - 50	0.9	0.08	0.7	< det	3.4
0 - 1	1.4	0.22	0.8	0.3	3.2
4 - 6	0.9	0.09	0.4	< det	1.2
8 - 10	0.7	0.09	0.4	0.2	1.1
25 - 30	0.8	0.21	0.8	< det	3.4
45 - 50	0.7	0.20	0.8	< det	3.2
Aluminum Elfhoeven					
0 - 50	2.1	0.10	0.7	< det	3.7
0 - 1	2.6	0.31	1.0	0.5	3.7
4 - 6	2.0	0.13	0.5	1.3	2.8
8 - 10	2.1	0.15	0.5	1.4	3.1
25 - 30	2.0	0.17	0.6	0.8	3.0
45 - 50	1.9	0.25	0.9	< det	3.0
detection limit = 0.05 % Al					

result in a far more uniform aluminum distribution in the sediments. This can be checked by further research.

The measured aluminum contents in the two lakes are low in comparison to those of lake Brielle (Hieltjes, 1980) to the contents measured in some lakes in the same area (Meijer, 1981) and to contents in lake- and river-sediments outside the Netherlands (table 37).

10.3 ARSENIC

Contents and comparison

Arsenic-contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 38. Some data of lake- and river-sediments from other sources are summarized in table 39.

Table 37.

Aluminum-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
4.1	10.1	L. Winnipeg	Allan and Brunskill	1977
0.81	9.54	Wisconsin lakes	Bortleson and Lee	1974
3	6	L. Windermere	Hamilton-Taylor	1981
3	5	L. Brielle	Hieltjes	1980
0.11	0.41	L. Westeinder	Meijer	1981
0.11	0.49	L. Nieuwe Meer	Meijer	1981
0.17	0.27	L. Nieuwkoop	Meijer	1981
0.30	0.40	L. Langeraar	Meijer	1981
0.51	0.59	L. Braassem 0-4 cm	Meijer	1981
0.41	0.42	L. Braassem >4 cm	Meijer	1981
0.52	3.60	Ohio R.	Spencer	1976

Discussion

The average arsenic contents in lake Westeinder and in lake Elfhoeven are 0.002 and 0.003 %. Arsenic is one of the most variable elements in the sediments of both lakes both in horizontal and in vertical direction. Due to this variation no three-dimensional structures could be detected.
Arsenic peaks of 0.014 % in core 5 (lake Westeinder) and 0.013 and 0.011 % in cores 28 and 30 (both lake Elfhoeven) are the largest concentrations of arsenic measured. In both lakes these occur occasionally at variable locations.

The decrease of the arsenic content of the Rhine sediments from 100 % (reference level) in 1960 to 66 % in 1970 (de Groot and Allersma, 1975) and about 40 % in 1978 (Salomons and Forstner, 1984), was not reflected by the arsenic contents in lake Westeinder and lake Elfhoeven. In several cases the toplayers of both sediments contain more arsenic than the deeper layers. In lake Elfhoeven the extreme arsenic concentrations occur at different depths and in different cores. This means that the largest concentrations can occur anywhere in the lake.

The only patterns that were found to exist for arsenic are that the arsenic contents of the toplayer of the sediments in the eastern part of lake Westeinder on some sampling locations 4, 5, 9, 10 and 16 are all below detection level and that the contents observed in the toplayer in the western and the central part of the lake are among the highest measured. This is consistent with the pattern found for copper. In the sedimentlayer between 4 and 6 cm below the sedi-

Table 38.

Arsenic-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Arsenic Westeinder					
0 - 50	0.002	0.000	0.002	< det	0.014
0 - 1	0.003	0.001	0.003	< det	0.009
4 - 6	0.003	0.001	0.002	< det	0.008
8 - 10	0.003	0.000	0.002	< det	0.007
25 - 30	0.002	0.000	0.002	< det	0.005
45 - 50	0.003	0.001	0.003	< det	0.014
Arsenic Elfhoeven					
0 - 50	0.003	0.000	0.003	< det	0.013
0 - 1	0.003	0.001	0.005	< det	0.013
4 - 6	0.003	0.001	0.002	< det	0.006
8 - 10	0.003	0.001	0.002	< det	0.005
25 - 30	0.003	0.001	0.002	< det	0.007
45 - 50	0.003	0.001	0.003	< det	0.011

detection limit = 0.0003 % As

ment water interface the concentration at the sampling locations at the southern shore (cores 1, 2, 3, 4, 11, 14 and 15) are somewhat higher than at the northern one (cores 8, 9, 12, 13 and 17)

In the northern part of the lake the arsenic-contents in the layer between 25 and 30 cm were often smaller than detection level. An extreme high arsenic value (0.014 % As) occurred in core 5 in the deepest sediment layer. No gradient was observed in the cores in the surroundings of this sampling location. A large difference in arsenic contents 0.001 and 0.013 % was found in two cores taken within a few meters distance. This shows that the horizontal distribution can only be observed on scales smaller than a few meters. This means that no structures of arsenic could be detected over the lake-area within the scale of sampling.

Arsenic concentrations of 0.003-0.03 % As were measured in sediments in the Danube, in lake Michigan and in the Elbe river by Petrovic (1981), Christensen (1981) and Lichtfuss (1981). In sediments sampled in the vicinity of mining operations and smelters arsenic concentrations reach levels of 0.03 % (Jonassen and Timperley, 1975). De Groot and Allersma (1975) report contents of 0.06 % arsenic in the Ems. A value

Table 39.

Arsenic-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference
% of dry weight	% of dry weight		
< 0.00003		Columbia R. (USA)	Brannon 1980
	0.0009	Branford Harbor	Brannon 1980
0.0001		L. Nelson	Crocket 1981
	0.0088	L. Fairbanks (Can)	Crocket 1981
0.0020	0.0073	Rhine river	Dissanayake 1983
	0.006	R. Ems	de Groot 1975
	0.022	R. Rhine	de Groot 1975
	0.03	Yellowknive district (USA)	Jonassen & Timperley 1975
	0.015	Hamburg Port (FRG)	Lichtfuss 1981
0.0017	0.0042	R. Pek	Petrovic 1981
0.0006	0.01	R. Drau	Teherani 1981

of 0.0022 % is measured in Rhine sediments. Teherani (1981) gives values of 0.0006 - 0.01 % As for sediments of the Drau river.

10.4 CALCIUM

Contents and comparison

Calcium contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 40. Some data of lake- and river-sediments from other sources are summarized in table 41.

Table 40.

Calcium-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Calcium Westeinder					
0 - 50	11.6	0.6	5.3	0.6	30.3
0 - 1	14.6	1.3	5.0	6.2	30.3
4 - 6	13.8	1.5	5.5	5.9	23.7
8 - 10	12.5	1.4	5.3	5.4	21.4
25 - 30	9.4	1.1	4.4	1.2	17.1
45 - 50	8.4	0.9	3.6	0.6	14.7
Calcium Elfhoeven					
0 - 50	7.9	0.2	1.2	0.8	11.2
0 - 1	8.4	0.2	0.6	7.2	9.1
4 - 6	8.3	0.2	0.6	7.1	9.2
8 - 10	8.0	0.2	0.7	0.8	9.3
25 - 30	7.7	0.5	1.7	5.5	11.2
45 - 50	6.8	0.4	1.5	5.0	9.1

detection limit = 0.004 % Ca

Discussion

Calcium is the fifth most abundant element in the earth crust, in both lake Westeinder and lake Elfhoeven it is the third most abundant one, most of it probably as CaCO3. The calcium concentrations in lake Westeinder are decreasing with depth (table 40), like was the case with copper but less pronounced. In lake Elfhoeven sediments, the calcium contents are more uniformly distributed, both in horizontal and in vertical direction. The maximum content in lake Westeinder sediments (30.3 %) is much higher than that in lake Elfhoeven (11.2 % Ca) and in all other lakes in the region (Meijer, 1981, Kroon, 1981) With a few exeptions, the results correspond fairly good with earlier research in both lakes (Meijer, 1981 and Kroon, 1981) as is shown in table 41.

Calcium contents of lake Elfhoeven are also about the same as Hieltjes measured in lake Brielle sediments (1980): 3-10 % Ca of the dry weight.

Table 41.

Calcium-contents in lake- and river-sediments

minimum conc. % of dry weight	maximum conc. % of dry weight	location	reference
1.1	10.6	L. Winnipeg (Can)	Allan and Brunskill 1976
2.4	44.3	Rotsee (Switserl.)	Bloesch 1974
3	10	L. Brielle	Hieltjes 1980
	ca. 0	Danish lakes	Kamp Nielsen 1974
3.2	23.6	L. Westeinder 0- 5 cm	Kroon 1981
3.9	7.2	L. Westeinder 5-15 cm	Kroon 1981
0.1	9.7	L. Nieuwkoop 0- 5 cm	Kroon 1981
0.7	6.3	L. Nieuwkoop 5-15 cm	Kroon 1981
6.2	7.4	L. Westeinder	Meijer 1981
1.9	2.6	L. Nieuwe Meer	Meijer 1981
1.9	5.0	L. Nieuwkoop	Meijer 1981
1.3	5.4	L. Langeraar	Meijer 1981
0.9	3.1	L. Braassem 0-4 cm	Meijer 1981
1.3	3.6	L. Braassem >4 cm	Meijer 1981
0.6	3.7	L. Reeuwijk 0-4 cm	Meijer 1981
1.6	4.0	L. Reeuwijk >4 cm	Meijer 1981
11	18	Alpine lakes	Michler 1980
1.4	36	Danube R.	Petrovic 1981

10.5 CHROMIUM

Contents and comparison

Chromium contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 42. Some data of lake- and river-sediments from other sources are summarized in table 43.

Table 42.

Chromium-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Chromium Westeinder					
0 - 50	0.023	0.001	0.005	< det	0.032
0 - 1	0.026	0.001	0.002	0.020	0.029
4 - 6	0.023	0.001	0.003	0.020	0.028
8 - 10	0.024	0.001	0.003	0.020	0.032
25 - 30	0.023	0.001	0.003	0.020	0.031
45 - 50	0.020	0.001	0.008	< det	0.024
Chromium Elfhoeven					
0 - 50	0.027	0.000	0.002	0.021	0.034
0 - 1	0.030	0.001	0.002	0.027	0.034
4 - 6	0.026	0.000	0.001	0.025	0.029
8 - 10	0.026	0.000	0.001	0.025	0.028
25 - 30	0.026	0.000	0.001	0.025	0.027
45 - 50	0.026	0.001	0.002	0.021	0.028

detection limit = 0.001 % Cr

Discussion

The average chromium concentration in both lakes is 0.023 resp. 0.027 % Cr. Chromium is very uniformly distributed in both lake bottoms (table 42). The toplayers contain some more chromium than the deeper layers in both lakebottoms but the decrease of the content with depth is small and in layers below 5 cm under the sediment surface the contents are about constant. Reasons for being constant can be a constant input to the lake or chromium had sufficient time to reach an equilibrium in vertical direction. In sediments of the Dutch lakes Marker and IJssel chromium concentrations of 0.004-0.033 % were found (Ente 1981a and 1981b). These chromium contents are about the same as the values measured in this study. Similar to our results, Ente measured the highest values in the toplayers of the sediment, possibly caused by enrichments during the last years.

Most values from other investigations are about the same as measured in this study. In ten lakes in Wisconsin (USA), Iskandar and Keeney (1974) measured up to 0.0049 % Cr in toplayers of the sediments. Petrovic (1981) found 0.001-0.013 % Cr in sediments of the Danube River. In sediments in the river Rhine 0.009-0.010 % Cr was measured, much more constant (Schleichert, 1975).

Table 43.

Chromium-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
0.006	0.020	L. Winnipeg (Can)	Allan and Brunskill	1977
0.001	0.003	*Gulf of Catania* (Ita., marine)	*Castragna*	*1982*
0.004	0.033	L. Marker	Ente	1981a
0.003	0.033	L. IJssel	Ente	1981b
	0.005	L. Wisconsin (USA)	Iskandar *& Keeney*	1974
0.005	0.019	R. Elbe	Mueller	1980a
	0.057	R. Neckar	Mueller	1980b
0.001	0.006	Casco Bay (USA)	Larsen	1983
		R. Elbe	Lichtfuss	1978
	0.026	Geesthacht (FRG)	*Lichtfuss*	*1981*
0.002	0.048	Bermuda (marine)	Lyons	1983
0.001	0.013	Danube R.	Petrovic	1981
	0.034	Danube R.	Petrovic and Schleichert	1981
0.015	0.020	L. Neagh (N. Ire)	Rippey et al	1982
0.009	0.010	R. Rhine	Schleichert	1975
0.005	0.009	Ohio R.	Spencer	1981

Comparable and higher values were found by Petrovic and Schleichert (1981): up till 0.034 % Cr in sediments of Danube and by Mueller (1980) in the Neckar: in 1974 and in 1979 amounts of 0.057 and 0.043 % Cr resp. A decrease in time occurs This is in contradiction to the observations in lake Westeinder and lake Elfhoeven, where slightly decreasing contents with depth were observed.

10.6 COBALT

Contents and comparison

Cobalt contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 44. Some data of lake- and river-sediments from other sources are summarized in table 45.

Table 44.

Cobalt-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Cobalt Westeinder					
0 - 50	0.003	0.000	0.002	< det	0.008
0 - 1	0.002	0.001	0.002	< det	0.008
4 - 6	0.003	0.001	0.002	< det	0.007
8 - 10	0.003	0.001	0.003	< det	0.007
25 - 30	0.003	0.001	0.002	0.001	0.007
45 - 50	0.002	0.000	0.002	< det	0.005
Cobalt Elfhoeven					
0 - 50	0.005	0.000	0.002	< det	0.008
0 - 1	*0.005*	*0.001*	0.002	*< det*	*0.008*
4 - 6	0.005	0.000	0.001	0.001	0.006
8 - 10	0.005	0.000	0.002	0.001	0.006
25 - 30	0.004	0.000	0.002	< det	0.006
45 - 50	0.004	0.000	0.002	< det	0.006

detection limit = 0.0005 % Co

Discussion

The cobalt concentrations in the two lakebeds vary from smaller than detection level to 0.008 % Co. The average cobalt-content of lake Westeinder is about half that of lake Elfhoeven sediments at all depths. Variation in lake Elfhoeven sediments however is less than in Westeinder sediments (table 44). No clear change of cobalt content with depth was observed. Concentrations below detection level occur at all depths exept the layers 25-30 cm in lake Westeinder 4-6 and 8-10 cm in lake Elfhoeven.

The cobalt-contents of both lake-sediments are not high as compared to measurements in other lakes and rivers as can be seen *from table* 45.

10.7 COPPER

Contents and comparison

Copper contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 46. The original data of this study are shown in table 48. Some data of lake- and river-sediments from other sources are summarized in table 47.

Table 45.

Cobalt-contents in lake- and river-sediments

minimum conc. % of dry weight	maximum conc. % of dry weight	location	reference	
0.0017	0.0043	L. Winnipeg	Allan and Brunskill	1977
	0.0258	Geesthacht (FRG)	Lichtfuss	1981
0.005	0.05	L. Kelly (Can)	Nriagu	1982 *
0.001	0.01	L. Lohi (Can)	Nriagu	1982 *
0.0005	0.01	L. Nelson (Can)	Nriagu	1982 *

* These lakes are situated within 30 km from the smelters of Sudbury, Ontario, Canada.

Discussion

The average copper content is 0.014 and 0.010 % Cu for lake Westeinder and Elfhoeven resp. The variation in copper content is fairly large, especially in the toplayer in lake Westeinder sediments (table 46).
A sharp decrease of the content with depth is observed just below the toplayer. In the deeper layers, both contents and variation are lower. This sharp decrease is observed in both lake-sediments. Recent local discharges can a.o. be the cause. In lake Westeinder, a horizontal structure was detected. Very high contents were mainly measured in the south-western part of the lake in the cores 2, 7, 8, 9, 12, 13, 14 and 17. These locations are close to the inlet of water from the Ringvaart channel, a boezemwater of the polder Haarlemmermeer. This suggests a copperbinding to the sediment, which is fast as compared to the mixing processes in the lake. In lake Elfhoeven sediments horizontal structure is not observed. The observed depth structure means that a policy of selective dredging in lake Westeinder till a restricted depth removes a substantial part of the copper in the sediments. Patterns of the distribution of copper are discussed in detail in chapter VI.

Maximum values measured in this study are smaller than many values that are measured in other lake-sediments. Most of those coppercontents range between 0.001 % (Spencer, 1981 and Dossis, 1981) and 0.028 % (Eysakkers, 1981 and Petrovic and Schleichert, 1981). The latter value was found in Rhine sediments. Sediments of lake Marker and lake IJssel contain 0.0004 and 0.0014 % Cu (Ente, 1981a and 1981b). Extreme high values up to 0.9 % were measured in an industrial area in Canada near the smelters of Sudbury (Nriagu, 1982). Iskandar reported coppercontents of 10 Wisconsin lakes in Madison (USA) varying from 0.0007-0.0531 % Cu of the dry weight. The maximum values are influenced by a coppersulphate treatment of 3 lakes to combat algae growth. The maxi-

Table 48.

Measured copper concentrations in the sediments

layer (cm)	0-1	4-6	8-10	25-30	45-50
core	**lake Westeinder sediments**				
1	0.015	--	0.008	0.008	0.005
2	--	0.020	--	0.005	0.004
3	0.016	0.007	0.007	--	--
4	0.018	0.014	--	--	0.009
5	0.038	0.027	0.023	0.008	0.007
6	0.014	--	--	0.005	0.004
7	0.030	--	0.020	0.008	0.009
8	--	0.014	0.011	0.006	0.008
9	0.042	0.016	0.010	0.008	0.008
10	0.014	0.013	0.009	0.007	0.008
11	0.015	0.006	0.007	0.007	0.008
12	0.080	0.022	0.015	0.008	0.008
13	0.059	0.013	0.008	0.007	0.007
14	0.077	0.007	0.009	0.007	0.006
15	0.035	0.008	0.010	0.006	0.008
16	0.018	0.011	0.011	0.006	0.005
17	0.040	0.006	0.007	0.007	0.006
core	**lake Elfhoeven sediments**				
18	--	0.007	0.007	0.007	0.007
19	0.014	0.007	0.007	0.006	0.006
20	0.034	0.012	0.023	0.009	0.009
21	0.016	0.007	0.009	0.008	0.008
22	0.020	0.007	0.007	0.006	0.005
23	0.013	0.012	0.018	0.009	0.008
24	0.014	0.009	0.008	0.012	0.011
25	0.026	0.009	0.010	0.010	0.009
26	0.014	0.008	0.008	0.008	0.008
27	0.023	0.008	0.009	0.008	0.009
28	0.022	0.008	0.008	0.009	0.008
29	--	0.006	0.007	0.006	--
30	0.014	0.006	0.006	0.006	0.006

mum content of untreated lakes is 0.0064 % Cu. The addition migrates through the sediments, which is reflected by the occurrence of a copper peak at a depth of 10-25 cm. Below this depth, the coppercontents decrease rapidly. No distribution in depth for any of the five elements -Zn, Cd, Pb, Cr and Ni- with regard to possible mutual influences was observed between lakes treated with CuSO4 and those who were not.

Eysakkers in addition, mentions values in soils in the Netherlands -as backgroundvalue- of 0.0005 - 0.0050 % Cu. Apart from the top 5 cm layer, where some enrichment has occurred the content in the two investigated lakebottoms in this study do not exceed these values very much. The copper concentrations in deeper layers are identical in both lakes, in contrast with for example calcium.

Table 46.

Copper-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Copper Westeinder					
0 - 50	0.014	0.002	0.015	0.004	0.080
0 - 1	0.034	0.006	0.022	0.014	0.080
4 - 6	0.013	0.002	0.006	0.006	0.027
8 - 10	0.011	0.001	0.005	0.007	0.023
25 - 30	0.007	0.000	0.001	0.005	0.008
45 - 50	0.007	0.000	0.002	0.004	0.009
Copper Elfhoeven					
0 - 50	0.010	0.001	0.006	0.005	0.034
0 - 1	0.019	0.002	0.007	0.013	0.034
4 - 6	0.008	0.001	0.002	0.006	0.012
8 - 10	0.010	0.001	0.005	0.006	0.023
25 - 30	0.008	0.001	0.002	0.006	0.012
45 - 50	0.008	0.000	0.002	0.005	0.011

detection limit = 0.0004 % Cu

10.8 IRON

Contents and comparison

Iron contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 49. Some data of lake- and river-sediments from other sources are summarized in table 50.

Table 47.

Copper-contents in lake- and river-sediments

minimum conc. % of dry weight	maximum conc. % of dry weight	location	reference	
0.001	0.0052	L. Winnipeg (Can)	Allan and Brunskill	1977
0.00003		Pencasola (USA)	Brannon	1980
	0.145	Bridgeport Harbor	Brannon	1980
0.0004	0.0025	Gulf of Catania (Ita., marine)	Castragna	1982
0.0025	0.0060	Stephens Creek Res. (Austral.)	Coggins	{_1979
0.0005	0.005	Soils in the Netherlands	Eysakkers	1981
0.0003	0.014	L. IJssel	Ente	1981a
		L. Wisconsin	Iskandar	1974
0.0007	0.0531	($CuSO_4$-treated)		
	0.0064	(untreated)		
0.0004	0.0045	Casco Bay (USA)	Larsen	1983
	0.0728	Geesthacht	Lichtfuss	1981
0.0005	0.0149	Bermuda (marine)	Lyons	1983
	0.9	L. Kelly	Nriagu	1982 *
	0.247	L. Nelson	Nriagu	1982 *
0.0043	0.018	R. Pek	Petrovic	1981
0.0035	0.028	R. Danube	Petrovic	1981
0.001	0.003	Ohio R.	Spencer	1981
	0.0038	Lough Neagh	Rippey	1982

* These lakes are situated within 30 km from the smelters of Sudbury, Ontario, Canada.

Discussion

The average Fe content in lake Westeinder is 2.45 %, the range being 0.1-4.63 %. No large variation in vertical direction was observed (table 49).
In horizontal direction the variation was considerable. The largest varations were measured in the toplayer of lake Westeinder and in the deepest layer in lake Elfhoeven (table 49).

Lake Elfhoeven sediments contain about 40 % more iron than lake Westeinder sediments. The ratio between maximim and minimum values in all other sediment layers of the Elfhoeven sediment was about 2, in lake Westeinder this ratio increased to 35, especially in the top-layers. The low iron concentration occurred incidentally in core 9 and 12. No significant change of the iron content with depth was observed in lake Westeinder nor in lake Elfhoeven. This is consistent with the observations of Meijer, who investigated two depths in some lake in the same area. The two layers are 0-5 cm which she assumes to be oxydized and 5-10 cm assumed to be reduced. The variation of the iron concentrations in horizontal direction in lake Westeinder was also found by Meijer (1981). Salomons and Gerritse (1981) found contents of 2.1-2.6 % Fe in sediments of the Dollard estuary. In deep Swiss lakes, iron contents of 0.33-5.0 % were measured by Bloesch (1974). In Stephans Creek Reservoir (Austr.), Long Lake (USA) and in Windermere sediments high iron contents up till 6 and 7.2 % were measured (Coggins, 1979 and Hamilton Taylor, 1979).
An exeptionally low iron content was measured in lake Pensacola (USA): 0.0014 % (Brannon, 1980).

Table 49.

Iron-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Iron Westeinder					
0 - 50	2.45	0.13	1.30	0.10	4.63
0 - 1	2.33	0.25	0.97	0.10	3.63
4 - 6	2.24	0.37	1.38	0.26	4.50
8 - 10	2.57	0.37	1.39	0.42	4.56
25 - 30	2.85	0.26	0.99	1.45	4.63
45 - 50	2.26	0.25	0.98	0.76	4.40
Iron Elfhoeven					
0 - 50	3.39	0.08	0.38	0.57	4.26
0 - 1	3.53	0.12	0.40	2.76	4.02
4 - 6	3.38	0.17	0.60	1.57	3.99
8 - 10	3.32	0.17	0.63	1.95	3.95
25 - 30	3.40	0.13	0.47	2.13	4.09
45 - 50	3.32	0.27	0.94	0.57	4.26

detection limit = 0.004 % Fe

The XRF-analyzing technique makes no distinction between Fe(II) and Fe(III). As iron compounds of phosphorus form a large part of phosphorus bound in sediments, it may be very useful to be able to distinguish between the oxidized and reduced state of iron. Investigations with Mossbauer Spectroscopy already demonstrated, that chemical distinction between forms in which phosphorus is bound in the sediments is uncertain, because of the assumed, but often not effective selectivity of the extraction procedures used (Siebers et al, 1982).

Table 50.

Iron-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
0.9	3.3	L. Winnipeg (Can)	Allan and Brunskill	1976
0.33	5.0	L. Vierwaldstatter (Switserland)	Bloesch	1974
0.71	6.95	Wisconsin lakes	Bortleson and Lee	1974
0.0014		Pensacola (USA)	Brannon	1980
	4.77	Branford Harbor	Brannon	1980
2.2	7.2	Stephens Creek Res. (Austral.)	Coggins	1979
0.1	0.4	Spencer Gulf (Australia)	Dossis	1981
	7.2	L. Windermere	Hamilton-Taylor	1979
0.2	4.0	L. Brielle	Hieltjes	1980
0.38	1.95	L. Westeinder	Kroon	1981
0.81	1.49	L. Nieuwkoop	Kroon	1981
	3.7	Hamburg Port (FRG)	Lichtfuss	1981
0.2	2.74	Bermuda (marine)	Lyons	1983
1.02	1.80	L. Kager (boezem)	Meijer	1981
2.22	2.23	*L. Braassem (boez)*	*Meijer*	*1981*
2.16	2.33	L. Braassem 0-4 cm	Meijer	1981
1.57	2.29	L. Braassem >4 cm	Meijer	1981
0.04	1.97	L. Westeinder	Meijer	1981
1.05	2.04	L. Nieuwe Meer	Meijer	1981
0.27	0.28	L. Reeuwijk	Meijer	1981
1.39	3.37	L. Reeuwijk 0-5 cm	Meijer	1981
1.02	3.09	L. Reeuwijk >5 cm	Meijer	1981
0.2	0.69	L. Nieuwkoop	Meijer	1981
0.65	1.22	L. Langeraar	Meijer	1981
0.001	0.06	Georges Bank (USA)	Piotrovic	1981
2.1	2.6	Dollard Estuary	Salomons and Gerritse	1981
1.12	3.34	Ohio R.	Spencer	1981
	6	Long Lake (USA)	Thomas	1977

10.9 LEAD

Contents and comparison

Lead contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 51. Some data of lake- and river-sediments from other sources are summarized in table 52.

Table 51.

Lead-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Lead Westeinder					
0 - 50	0.010	0.001	0.009	< det	0.036
0 - 1	0.004	0.002	0.008	< det	0.027
4 - 6	0.010	0.003	0.010	< det	0.031
8 - 10	0.014	0.003	0.011	< det	0.036
25 - 30	0.014	0.002	0.006	< det	0.028
45 - 50	0.011	0.002	0.007	< det	0.024
Lead Elfhoeven					
0 - 50	0.021	0.003	0.024	< det	0.154
0 - 1	0.008	0.005	0.016	< det	0.051
4 - 6	0.023	0.007	0.021	< det	0.108
8 - 10	0.021	0.002	0.007	0.012	0.031
25 - 30	0.031	0.011	0.039	0.008	0.154
45 - 50	0.019	0.003	0.011	0.004	0.036

detection limit = 0.005 % Pb

Discussion

The average leadcontents in lake Westeinder and lake Elfhoeven sediments are 0.01 and 0.021 % Pb. Toplayers of the sediment contain the lowest average values. Leadconcentrations in lake Elfhoeven sediments are twice as high as in lake Westeinder both in the toplayer and at greater depth. In lake Westeinder the contents are increasing just below the sediment surface and than remain constant at the level of about 0.010-0.015 % Pb. This can be caused by a decrease of the input. Replacement of lead by copper tubes in houses for drinking water supply can have contributed to this.

In lake Elfhoeven some incidental peaks were found. In one core at two different depths a peak was observed: 0.108 % Pb (4-6 cm) and 0.154 % Pb (25-30 cm). The maximum measured in lake Elfhoeven was also observed by Teherani in the river Drau (1981): 0.12 % Pb. Incidental high values were also found by Nriagu, 1982.

Iskandar measured leadconcentrations in 10 lake sediments in the USA, that varied from smaller than detection limit (0.1 ppm) to 0.0167 % Pb. Ente gives values of 0.0004-0.023 % Pb for sediments in the dutch lake Marker and lake IJssel

Table 52.

Lead-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
0.0002	0.0278	L. Winnipeg (Can)	Allan and Brunskill	1976
0.00003		Pensacola (USA)	Brannon	1980
	0.052	Branford Harbor	Brannon	1980
0.0005	0.0019	Gulf of Catania (Italy, marine)	Castragna	1982
0.003	0.065	Stephens Creek Res. (Austral.)	Coggins	1979
0.0010	0.0013	Spencer Gulf (Australia)	Dossis	1981
0.0004	0.023	L. Marker	Ente	1981a
0.0	0.0167	L. Wisconsin	Iskandar	1974
0.0009	0.0061	Casco Bay (USA)	Larsen	1983
	0.0385	Hamburg Port (FRG)	Lichtfuss	1981
0.0002	0.0229	Bermuda (marine)	Lyons et al	1983
0.003	0.016	L. Ramsey (Can)	Nriagu	1982
0.0	0.116	L. Nelson	Nriagu	1982
	0.0031	Lough Neagh	Rippey	1982
0.0012	0.0067	Ohio R.	Spencer	1981
0.0069	0.12	R. Drau	Teherani	1981
0.016	0.031	L. Brielle	Zschuppe	1974

(1981a and 1981b). The values that Zschuppe (1974) gives for lake Brielle are lower than the high values of lake Elfhoeven, but are of the same order as in lake Westeinder sediments: 0.016-0.031 % Pb. Rolfe and Jennett (1975) compared Pb-depth profiles of urban and rural soils. The contents of the upper 10 cm were 0.039 and 0.0016 % Pb resp. Deeper in the sediment (30-40 cm) the contents are 0.0040 and 0.0006 % Pb.

Sources of lead pollution are a.o. wastewater discharges and atmospheric fallout. The latter causes an annual deposition of about 1000 tons of lead into the North Sea (Foerstner, 1978). De Groot and Allersma (1975) calculated the ratio for Pb contents in Rhine sediments in 1970 to those in 1960 as 0.85. The same decrease with time and thus to a certain extent with depth can be concluded from the data in this study. Arsenic even decreased more dramatically in the Rhine, but this was not observed in the depth profiles. Lead as tube material used in drinking water supply is replaced by copper more and more since the sixties. This may also have contributed to the increased coppercontents in the toplayers of the sediments. The decrease in the use of lead is consistent with the lower lead contents in the toplayer of the sediments of both lakes.

10.10 MAGNESIUM

Contents and comparison

Magnesium contents in the sediments of lake Westeinder and *lake Elfhoeven are shown in table 53. Some data of lake-* and river-sediments from other sources are summarized in table 54.

Table 53.

Magnesium-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Magnesium Westeinder					
0 - 50	0.09	0.01	0.09	< det	0.41
0 - 1	0.05	0.03	0.11	< det	0.36
4 - 6	0.08	0.02	0.07	< det	0.19
8 - 10	0.09	0.01	0.05	< det	0.17
25 - 30	0.11	0.03	0.10	< det	0.41
45 - 50	0.10	0.02	0.09	< det	0.38
Magnesium Elfhoeven					
0 - 50	0.23	0.02	0.12	< det	0.53
0 - 1	0.18	0.06	0.19	< det	0.53
4 - 6	0.27	0.02	0.08	0.11	0.38
8 - 10	0.27	0.02	0.08	0.13	0.39
25 - 30	0.23	0.03	0.10	0.11	0.41
45 - 50	0.22	0.02	0.10	0.05	0.42
detection limit = 0.017 % Mg					

Table 54.

Magnesium-contents in lake- and river-sediments

minimum conc. % of dry weight	maximum conc. % of dry weight	location	reference	
0.6	5.2	L. Winnipeg (Can)	Allan and Brunskill	1977
0.5	1.5	L. Brielle	Hieltjes	1980
0	3	L. Valencia (Sp.)	Lewis	1981
0.1	2	Ammersee	Michler	1980
0.26	0.96	Ohio R.	Spencer	1981

Discussion
The magnesiumcontents in both lakebottoms reach from smaller than detection limits to 0.41 and 0.53 % Mg resp. as is shown in table 53 The average magnesium concentration in lake Elfhoeven sediments is two- to fourfold that in lake Westeinder on each of the five analysed sediment depths. This was also the case with the aluminum content (table 36). this could not be explained so far. Concentrations smaller than detection limits occur at every depth in lake Westeinder, in lake Elfhoeven only in the toplayer. The range of the observations is very high as a consequence.

In both lakes the magnesium content of the toplayer is lower than that of any of the deeper layers but the scatter in both toplayers is higher. This may be due to local downward transport processes and correlate with locally higher infiltration velocities for example in the south-western part of lake Westeinder, as was also shown when copper was discussed. Correlation with other elements can become important now. Magnesium is significantly correlated with many elements in both lakes. The existence of negative correletion with copper, significant at the 5 % level, indicates that the high copper concentrations in the south-western part of lake Westeinder can correlate with low magnesium concentrations in the toplayer in same area. This however is not the case.

Accumulation in deeper layers occurred in some cases (core 2, 3, 11, 14 and 17), but not all low values in the toplayer correlate with accumulated magnesium in deeper layers. The magnesium contents in both lake Westeinder as lake Elfhoeven are low compared to the contents, measured in other investigations. Hieltjes (1980) measured 0.5-1.5 % Mg in lake Brielle sediments. This may very well be caused by the fact that in 1950 the direct connection of lake Brielle to the north sea was closed by dam. Spencer (1981) measured about the same range of values: from 0.2 to 1.2 % Mg. Higher values were often observed by several authors (table 54)

10.11 MANGANESE

Contents and comparison
Manganese contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 55. Some data of lake- and river-sediments from other sources are summarized in table 56.

Table 55.

Manganese-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Manganese Westeinder					
0 - 50	0.22	0.01	0.11	< det	0.48
0 - 1	0.19	0.03	0.12	< det	0.35
4 - 6	0.20	0.03	0.12	< det	0.37
8 - 10	0.23	0.04	0.13	0.02	0.48
25 - 30	0.23	0.02	0.08	0.05	0.32
45 - 50	0.22	0.02	0.09	0.04	0.36
Manganese Elfhoeven					
0 - 50	0.11	0.01	0.03	0.04	0.17
0 - 1	0.09	0.01	0.03	0.04	0.15
4 - 6	0.13	0.01	0.03	0.08	0.17
8 - 10	0.12	0.01	0.02	0.08	0.15
25 - 30	0.11	0.01	0.02	0.06	0.13
45 - 50	0.10	0.01	0.03	0.06	0.15

detection limit = 0.001 % Mn

Table 56.

Manganese-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
0.038	0.165	L. Winnipeg (Can)	Allan and Brunskill	1977
0.021	0.402	Wisconsin lakes	Bortleson and Lee	1974
0.006	0.08	Seine (France)	Boust	1981
0.00004		Pensacola (USA)	Brannon	1980
	0.096	Houston Ship Channel (USA)	Brannon	1980
0.034	0.142	Stephens Creek Res. (Austral.)	Coggins	1979
0.4	1.82	L. Windermere	Hamilton-Taylor	1979
	0.136	Hamburg Port (FRG)	Lichtfuss	1981
0.0025	0.13	R. Pek	Petrovic	1981
0.041	0.164	Ohio R.	Spencer	1981
0.023	0.026	Drau R.	Teherani	1981

Discussion

The average manganese content of the sediments in lakes Westeinder and Elfhoeven are 0.22 and 0.11 resp., the content in lake Westeinder being two times as high as in lake Elfhoeven. The variation with depth is only small. Horizontal variation of the manganese concentrations is considerable, especially in lake Westeinder.

In Windermere sediments manganese values of 0.4-1.82 % were measured (Hamilton-Taylor, 1979), much higher than both lake Westeinder and lake Elfhoeven. Mizobuchi (1980) and Teherani (1981) observed lower concentrations than in this study. Thomas and Soltero (1977), Lichtfuss (1978) Allan and Brunskill (1977) measured about the same manganese concentrations as we did. The range of the observations is a little smaller than in lake Westeinder. Petrovic (1981) and Coggins (1979) did observe values which are very much alike those of lake Elfhoeven.

10.12 MERCURY

The mercury content was below detection-level of 0.0020 % Hg in all samples in both lake Westeinder and lake Elfhoeven.

10.13 NICKEL

Contents and comparison

Nickel contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 57. Some data of lake- and river-sediments from other sources are summarized in table 58.

Table 57.

Nickel-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Nickel Westeinder					
0 - 50	0.002	0.000	0.001	< det	0.004
0 - 1	0.002	0.000	0.001	< det	0.004
4 - 6	0.002	0.000	0.001	< det	0.004
8 - 10	0.002	0.000	0.001	< det	0.004
25 - 30	0.002	0.000	0.001	< det	0.004
45 - 50	0.001	0.000	0.001	< det	0.003
Nickel Elfhoeven					
0 - 50	0.003	0.000	0.001	< det	0.004
0 - 1	0.003	0.000	0.001	0.002	0.004
4 - 6	0.003	0.000	0.001	0.001	0.004
8 - 10	0.003	0.000	0.001	0.002	0.004
25 - 30	0.003	0.000	0.001	0.001	0.004
45 - 50	0.003	0.000	0.001	< det	0.004

detection limit = 0.0003 % Ni

Table 58.

Nickel-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
0.003	0.008	L. Winnipeg (Can)	Allan and Brunskill	1977
0.001	0.003	Rhone R.	Added	1980
0.0005	0.005	Soils in the Netherlands	Eysakkers	1981
0.0001	0.006	L. Wisconsin	Iskandar	1974
0.0005	0.0032	Casco Bay (USA)	Larsen	1983
0.007	0.017	Neckar	Lichtfuss	1978
	0.0090	Hamburg Port (FRG)	Lichtfuss	1981
	0.24	L. Nelson (Can)	Nriagu	1982 *
	1.2	L. Kelley (Can)	Nriagu	1982 *
0.001	0.006	Danube R.	Petrovic	1981
0.01	0.02	L. Neagh (N. Ire)	Rippey	1982

* These lakes are situated within 30 km from the smelters of Sudbury, Ontario, Canada.

Discussion

The average nickel concentrations in both lakebottoms is quite constant: in lake Westeinder and lake Elfhoeven 0.002 and 0.003 % Ni resp. The contents range from 0.0-0.004 % Ni. In vertical direction no significant differences in concentrations were observed as can be seen from table 57. Nickel contents smaller than detection limit occurred in lake Westeinder at every depth, but only on one deep location in lake Elfhoeven (core 22).

The measured values in this study are about the same as in sediments of the Danube River: 0.001-0.006 % Ni (Petrovic, 1981) and sediments from the Rhone: 0.001-0.003 % Ni (Added, 1980).
With respect to sediments from Neckar the values in this study are lower: Lichtfuss (1978) measured 0.007-0.017 % Ni. Eysakkers (1981) gives data of 0.0005-0.0050 % Ni for soils in the Netherlands.

10.14 PHOSPHATE IN THE SEDIMENTS

Contents and comparison

Phosphate concentrations in the sediments of lake Westeinder and lake Elfhoeven are shown in table 59.The original data of this study are sho wn in table 61. Some data of lake- and river-sediments from other sources are summarized in table 60.

Table 61.

Measured phosphate concentrations in the sediments

layer (cm)	0-1	4-6	8-10	25-30	45-50
core	lake Westeinder sediments				
1	1.69	1.00	0.97	0.67	0.35
2	0.83	0.59	0.59	0.38	--
3	0.82	0.70	0.67	--	--
4	1.78	0.98	0.91	0.77	--
5	1.14	0.73	0.46	0.59	0.62
6	--	1.09	0.89	0.48	0.45
7	1.60	1.71	1.46	0.61	--
8	1.61	0.59	0.36	0.53	--
9	0.59	0.23	0.42	0.52	0.52
10	1.58	1.15	1.03	2.77	--
11	1.84	0.53	0.62	0.57	--
12	0.24	0.15	0.16	0.37	0.51
13	1.50	0.58	0.63	0.54	0.53
14	1.10	0.74	0.66	0.53	0.33
15	1.32	0.77	0.80	0.61	0.48
16	1.80	1.53	1.42	0.93	0.88
17	0.44	0.46	0.47	0.44	--
core	lake Elfhoeven sediments				
18	1.14	0.95	0.87	0.63	--
19	1.26	0.98	0.84	0.73	0.69
20	0.90	0.44	0.56	0.69	0.84
21	1.04	0.84	0.99	0.82	0.57
22	1.01	1.01	0.94	0.38	0.27
23	1.63	1.38	0.69	0.64	0.66
24	1.27	1.12	1.09	1.21	1.10
25	1.30	1.01	1.09	0.91	0.83
26	1.45	1.16	1.03	0.92	0.99
27	1.08	1.11	0.83	0.65	0.81
28	1.28	0.99	0.99	0.86	0.67
29	1.03	1.04	0.96	--	--
30	1.42	1.11	1.01	0.87	--

Discussion

A detailed discussion on phosphorus in the sediments and interstitial water is given in chapter VII. The average phosphorus content of all sampling points is 0.082 and 0.084 % P on basis of dry weight in Westeinder and Elfhoeven sediments resp. The maximum contents are measured in the utmost toplayer of the sediments in both lakes. A sharp decrease just below the toplayer changes to a gradual decrease with depth and the content stabilizes at depths of 10-40 cm. Similar depth profiles were observed for total-phosphate concentrations in the interstitial water at depths larger than about 30 cm. This suggests equilibrium situations at depths of 30 cm and more. The observed structures of phosphorus in the sediments will further be discussed in chapter VII.

Table 59.

Measured phosphate concentrations in the sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Phosphorus Westeinder					
0 - 0.5	0.119	0.014	0.052	0.024	0.184
0.5 - 1	0.124	0.013	0.050	0.024	0.184
1 - 2	0.116	0.011	0.045	0.016	0.184
2 - 3	0.097	0.010	0.041	0.021	0.179
3 - 4	0.084	0.010	0.042	0.021	0.175
4 - 6	0.080	0.010	0.040	0.015	0.171
6 - 8	0.079	0.008	0.034	0.015	0.131
8 - 10	0.074	0.008	0.034	0.016	0.146
10 - 15	0.072	0.008	0.035	0.018	0.179
15 - 20	0.069	0.008	0.033	0.031	0.172
20 - 25	0.061	0.004	0.017	0.040	0.100
25 - 30	0.071	0.014	0.055	0.037	0.277
30 - 35	0.056	0.004	0.016	0.037	0.092
35 - 40	0.057	0.004	0.017	0.037	0.096
40 - 45	0.059	0.006	0.023	0.026	0.109
45 - 50	0.052	0.004	0.015	0.033	0.088
Phosphorus Elfhoeven					
0 - 0.5	0.122	0.006	0.020	0.090	0.163
0.5 - 1	0.122	0.006	0.020	0.090	0.163
1 - 2	0.116	0.006	0.023	0.085	0.161
2 - 3	0.107	0.004	0.016	0.071	0.136
3 - 4	0.105	0.005	0.017	0.070	0.126
4 - 6	0.101	0.006	0.021	0.044	0.138
6 - 8	0.089	0.004	0.014	0.056	0.113
8 - 10	0.091	0.004	0.015	0.056	0.109
10 - 15	0.080	0.003	0.012	0.054	0.100
15 - 20	0.076	0.004	0.013	0.056	0.099
20 - 25	0.077	0.004	0.015	0.067	0.114
25 - 30	0.078	0.006	0.020	0.038	0.121
30 - 35	0.074	0.005	0.018	0.044	0.118
35 - 40	0.077	0.006	0.020	0.041	0.115
40 - 45	0.071	0.006	0.021	0.028	0.107
45 - 50	0.074	0.007	0.022	0.027	0.110

10.15 TOTAL-PHOSPHATE IN THE INTERSTITIAL WATER

Contents and comparison

The total-phosphate concentrations of the intestitial water in the sediments of lake Westeinder and lake Elfhoeven are shown in table 62.

Table 60.

Phosphate concentrations in lake and river-sediments

minimum conc.	maximum conc.	location	reference
% of dry weight	% of dry weight		
0.01	0.07	L. Winnipeg	Allan and Brunskill 1977
0.03	0.36	Vierwaltst. See	Bloesch 1974
0.09	1.65	Wisconsin lakes	Bortleson and Lee 1974
	0.12	L. Mohegan (aver.)	Fillos and Biswas 1976
0.1	0.3	L. Peris and L. Padarns (N. Irl.)	Guppy 1978
0.2	0.5	L. Brielle	Hieltjes 1980
0.05	0.25	L. Glumso	Jorgensen 1975
0.1	0.3	Danish Lakes	Kamp Nielsen 1978
0.03	0.13	L. Westeinder	Kroon 1981
0.07	0.12	L. Nieuwkoop	Kroon 1981
0.08	0.12	L. Valencia (Sp)	Lewis 1981
0.027	0.093	L. Elfhoeven	Meijer 1981
0.04	0.15	L. Kager	Meijer 1981
0.145	0.197	L. Braassem	Meijer 1981
0.123	0.342	Nieuwe Meer	Meijer 1981
0.423	0.436	L. Reeuwijk	Meijer 1981
0.024	0.075	L. Nieuwkoop	Meijer 1981
0.063	0.838	L. Langeraar	Meijer 1981
0.08	0.25	L. Neagh (N. Irl.)	Rippey 1982
0.07	0.17	Dollard Estuarine	Salomons and Gerritse 1981
0.04	0.08	Rhine R.	Schleichert 1975

Some total-phosphate concentrations in interstitial waters of lake- and river-sediments from other sources are summarized in table 63.

Discussion

In both lakes the total-phosphate concentrations show very large differences with depth and with the sampling location. The average concentration in lake Westeinder is about four times that of lake Elfhoeven: 4.07 mgP/l and 1.08 mgP/l resp. The scatter in the observations in lake Westeinder is larger than in lake Elfhoeven, suggesting a more dynamic behaviour.

The maximum individual and average concentrations in both lake Westeinder and lake Elfhoeven occur at depths varying from 3-25 cm. This is at variance with observations of Freedman and Canale (1977) who found the maximum values in the upper cm, but from profiles measured in the Bodensee, it appears that the position of the maximum in the profile is

Table 62.

Total-phosphate concentration in interstitial water

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	mg P/l				
Total-phosphate Westeinder					
0 - 50	4.07	0.39	5.98	0.30	44.55
0 - 0.5	1.79	0.27	1.06	0.57	4.98
0.5 - 1	2.46	0.48	1.88	0.38	5.93
1 - 2	3.37	0.77	2.89	0.50	9.15
2 - 3	3.06	0.76	2.93	0.68	9.45
3 - 4	3.77	0.87	3.49	0.75	13.70
4 - 6	3.94	0.99	3.95	0.41	12.40
6 - 8	4.47	1.16	4.65	0.49	16.80
8 - 10	4.05	1.00	3.99	0.56	14.80
10 - 15	4.78	1.83	7.32	0.30	30.53
15 - 20	6.09	2.72	10.87	0.71	44.55
20 - 25	6.16	2.90	11.24	0.64	44.55
25 - 30	5.54	2.52	9.74	1.05	37.95
30 - 35	4.56	1.67	6.46	0.94	22.88
35 - 40	4.60	1.38	5.35	1.31	21.38
40 - 45	3.19	0.95	3.28	0.94	13.20
45 - 50	2.21	0.33	1.05	0.87	4.85
Total-phosphate Elfhoeven					
0 - 50	1.08	0.07	0.93	0.25	6.53
0 - 0.5	1.31	0.41	1.35	0.28	4.38
0.5 - 1	0.90	0.26	0.85	0.25	3.20
1 - 2	1.18	0.19	0.70	0.40	2.33
2 - 3	1.11	0.23	0.82	0.44	3.15
3 - 4	1.27	0.49	1.69	0.25	6.53
4 - 6	1.25	0.41	1.47	0.40	4.23
6 - 8	1.17	0.24	0.88	0.46	3.75
8 - 10	1.30	0.30	1.05	0.25	3.95
10 - 15	1.09	0.28	1.02	0.25	3.83
15 - 20	1.12	0.24	0.84	0.35	3.15
20 - 25	1.09	0.22	0.81	0.36	2.34
25 - 30	0.86	0.18	0.64	0.26	2.15
30 - 35	0.84	0.17	0.57	0.33	2.20
35 - 40	0.89	0.15	0.51	0.35	1.95
40 - 45	0.90	0.15	0.50	0.36	1.71
45 - 50	0.99	0.19	0.60	0.47	1.65

rather varying (Frevert, 1979b). This is also appearant from Nriagu and Dell (1974): peaks occur at depths of 0 to 20 cm. Differences in the influence of the lakewater can cause

Table 63.

Total-phosphate in interstitial water

minimum conc.	maximum conc.	location	reference
mg P/l	mg P/l		
2	5.5	White L.	Freedman and Canale 1977
0.75	3.15	L. Constance	Frevert 1977
1.8	17	L. Westeinder	Kroon 1981
0.38	1.7	L. Nieuwkoop	Kroon 1981
0.02	0.38	L.Erie	Nriagu and Dell 1974

this. This implicitly suggests hypotheses about rates of transport, binding and exchange of phosphates in the sediments. Dynamic, not equilibrated processes can be the reason that the concentrations are very variable This is qualitatively dealt with in chapter VII. Some remarks on the observed data are given below.
In cores 5, 10 and 16 the total-phosphate concentration is increasing with depth. Maximum concentrations occur at depths varying from 15 cm (core 16) to 30 cm (core 5). In lake Elfhoeven this increase with depth is not observed. In cores 1, 7, 12 and 13, all from lake Westeinder, the high total phosphate concentrations in the toplayers are followed by a dip at depths of 1 to 4 cm and an increase again with depth (core 1) or more stable contents with depth (cores 7, 12 and 13). High concentrations in the toplayers were also measured in lake Elfhoeven in cores 18, 24 and 30, in core 24 and 30 again followed by a dip in concentration and an increase with increasing depth.
Low concentrations in the toplayers followed by a single peak were observed in lake Elfhoeven in cores 23 and 26.

In nearly all cores the contents are about constant at depths lower than 30 cm. Two exeptions are core 1, where the total-phosphate concentration further decreases with depth and core 5 where the constant concentration is only reached at about 40 cm depth. In several cases (cores 6, 8, 11, 12 and 14) the constant concentration is reached at depths between 5 and 10 cm (core 7, 9, 13 and 17).

In all cases the concentrations are strongly varying with depth and from sampling point to sampling point in a way that suggests very complex chemical processes. The interstitial water concentrations may be a snapshot of different stages of the processes in the sediments: the time scale of the processes that underlay these profiles, can be the same, but the time of the observation of the profiles gives an impression of the actual state of the system of for instance the movement of phosphates through the sediments. A rapid phosphate movement through the sediments was also measured by Hynes and Greib (1970) and between phosphate and plants by Ulrich et al (1962) with 32-P experiments. It appears that the profiles are not stable in time. Calculations on the time scales of the processes involved are made in the last section of chapter VII and is in the order of less than 1 to 3 years

The standard deviation in the toplayers is lower than in the deeper layers. This may be caused by a considerable influence of the water in the lake on the toplayers of the sediments.
In the layers deeper than 30 cm in the sediment the total-phosphate concentration of the interstitial water is about constant. This is also consistent with the diminishing influence or absence of processes like for instance bioturbation in absence of oxygen and less direct influence of loading from the surface water. In the layers in between the top and 30 cm depth, the processes are very complicated and locally strongly variable.

10.16 ORTHO-PHOSPHATE IN THE INTERSTITIAL WATER

Contents and comparison

Ortho-phosphate concentrations in the interstitial water of the sediments of lake Westeinder and lake Elfhoeven are shown in table 64. Some ortho-phosphate concentrations in lake- and river-sediments from other sources are summarized in table 65.

Discussion

The average ortho-phosphate content of the interstitial water of lake Westeinder sediments are about five times those of lake Elfhoeven again, like with the total-phosphate concentrations. High concentrations occur at varying depths. The ortho-phosphate concentrations are about the same as earlier measured in the toplayers in lake Westeinder (Meijer, 1981 and Kroon, 1981), those of lake Brielle (Hieltjes, 1980) and of several other lakes in the north-western part of the Netherlands (van Liere et al, 1983). Some remarks on the figures can be given. A low ortho-phosphate concentration in the upper layer followed by a high content, a dip and an increased concentration again is observed in the cores 1,3 and 9 in lake Westeinder. This shape of the profile was not observed in lake Elfhoeven. Low contents that hardly vary with depth were observed in the cores 2, 7, 8, 14 and 17 in lake Westeinder and in core 20 to 25, 27 and 28 in lake Elfhoeven. Some more remarks on this are made in chapter VII in the section retention and transport of phosphate in sediments.

A low concentration in the toplayer of 3 cm thickness, 1-2 mgP/l, is followed by a high content, 5 mg P/l, constant from 3-50 cm, is observed in core 16. All other profiles include concentration peaks of up to 13 mg P/l at different depths, varying from 0-10 cm (cores 11, 13) to 30-40 cm (cores 5, 10, 12). In lake Elfhoeven the concentration peaks are much lower (to 3 mg P/l) but also at varying depths.

Table 64.

Ortho-phosphate concentration in interstitial water

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	mg P/l				
Ortho-phosphate Westeinder					
0 - 50	2.65	0.38	5.90	0.06	12.80
0 - 0.5	1.10	0.14	0.55	0.11	1.98
0.5 - 1	1.46	0.28	1.08	0.11	4.10
1 - 2	1.75	0.57	2.14	0.28	8.85
2 - 3	2.16	0.62	2.48	0.34	8.65
3 - 4	2.80	0.83	3.42	0.32	7.10
4 - 6	2.41	0.55	2.20	0.46	7.88
6 - 8	3.02	0.89	3.58	0.49	11.50
8 - 10	2.88	0.88	3.62	0.57	12.80
10 - 15	2.76	0.68	2.71	0.32	8.95
15 - 20	2.74	0.70	2.89	0.26	8.75
20 - 25	2.48	0.67	2.66	0.26	9.40
25 - 30	2.40	0.65	2.61	0.14	10.00
30 - 35	2.15	0.41	1.62	0.22	5.85
35 - 40	2.34	0.60	2.31	0.14	9.70
40 - 45	1.74	0.31	1.07	0.06	4.70
45 - 50	1.83	0.35	1.09	0.83	4.75
Ortho-phosphate Elfhoeven					
0 - 50	0.54	0.05	0.74	0.01	2.67
0 - 0.5	0.35	0.09	0.30	0.02	1.01
0.5 - 1	0.31	0.09	0.32	0.02	1.21
1 - 2	0.48	0.16	0.56	0.01	2.25
2 - 3	0.50	0.11	0.41	0.01	1.25
3 - 4	0.43	0.11	0.39	0.02	1.04
4 - 6	0.43	0.17	0.60	0.02	2.34
6 - 8	0.57	0.12	0.43	0.03	1.42
8 - 10	0.62	0.18	0.63	0.02	2.14
10 - 15	0.49	0.18	0.66	0.01	2.12
15 - 20	0.58	0.19	0.68	0.03	2.67
20 - 25	0.70	0.21	0.74	0.02	2.20
25 - 30	0.40	0.09	0.30	0.01	1.01
30 - 35	0.59	0.17	0.58	0.02	2.11
35 - 40	0.42	0.10	0.34	0.11	1.23
40 - 45	0.50	0.16	0.54	0.06	1.70
45 - 50	0.62	0.16	0.50	0.16	1.57

10.17 ORGANIC PHOSPHATE IN THE INTERSTITIAL WATER

The difference between the total-phosphate and the ortho-

Table 65.

Ortho-phosphate concentration in interstitial water

minimum conc. mg P/l	maximum conc. mg P/l	location	reference	
0.5	15	L. Sodra Bergund.	Bengtsson	1975
1	14	L. Asejire (Nigeria)	Egborge	1981
2	4	White L.	Freedman and Canale	1977
0.38	28	L. Brielle	Hieltjes	1980
1.6	16	L. Westeinder	Kroon	1981
0.3	1.1	L. Nieuwkoop	Kroon	1981
0	15	L. Uitgeester	van Liere	1983
0	1	L. IJssel	van Liere	1983
1	8	Holysloter Die	van Liere	1983
0	2	L. Kortenhoef	van Liere	1983
0	1	L. Ankeveen	van Liere	1983
1.4	7.1	L. Westeinder	Meijer	1981

phosphate concentrations in the interstitial water, often called dissolved organic phosphates (Standard Methods Water and Wastewater, 1980), is varying every core but some groups of cores can be distinguished. In the cores 8, 9, 12, 13, 14 and 17 the difference between total- and ortho-phosphate is small at all depths (smaller than 1 mgP/l. In lake Elfhoeven this is the case in the cores 19, 22, 25, 27 and 28.

Low differences in the toplayers followed by larger amounts in deeper layers suggest deposits of organic material some time ago. This is observed in core 6, 15, 20, 23 and 26. Extreme amounts of probably organic phosphates occur in the cores 5 and 10. High organic phosphate in the toplayers followed by a decrease to a low level or a dip in the concentrations with increasing depth are observed in the cores 1, 7, 8, 24 and 30.

Over 90 % of the phosphorus in lakewater is bound organically in phosphate form and cellular constituents (Wetzel 1975). We did not measure this organic cellular material but we found an average of 36 % (lake Westeinder) and 54 % (lake Elfhoeven) of the total-phosphate to be organic.

In most cases however, the interstitial water does not contain much dissolved organic phosphate. In eleven cores out of thirty the concentrations are smaller than 1 mgP/l at all depths. In five cores in lake Westeinder and in three cores in lake Elfhoeven the organic-phosphates in the water of the sediments is high: cores 5, 6, 10, 15 and 16 and in the cores 20, 24 and 30. These high values are immediately followed by a sharp decrease with depth to less than 0.5 mgP/l

in all cases within 1 cm depth, thus suggesting either a rapid mineralization of organic material or a rapid dilution of the organic interstitial content due to infiltrating lakewater.
The observed larger concentrations of organic phosphate at different depths can be the reflection of other stages in time and or location of the same process: organic phosphate can be transported to deeper layers with downward percolating lakewater.

10.18 DISCUSSION ON INTERSTITIAL WATER PHOSPHATES

As was shown in the preceeding the concentrations of all interstitial water phosphates vary considerably with depth and with the location in the lake, much more than was the case with the phosphate concentrations in the sediments. Some general remarks can be made on the observed interstitial water concentration profiles.

(-) The concentration profiles do not seem to show any relation to the sampling location
(-) The concentrations in the deep sediment layers (from about 30 cm depth) are more or less constant, in both lakes in nearly all cores.
(-) The phosphate concentrations in the interstitial water in the sediment layer from the solid-water interface down to max. 30 cm, are very variable. Concentration differences of a factor 5 within one core are observed more than once.

From this it can be concluded, that the transport processes in the upper part of the sediments are much more rapid than deeper in the sediment. It may be that the constantness of the phosphate concentration deep in the sediments is also determined by the processes that took place in the toplayers and the infiltration of water through the sediments. This is confirmed by the correlations between soluble phosphate and total phosphate in the solid sediment that is only positively significant in the deeper layers of lake Westeinder sediments. From this it can be concluded that it may be useless to sample porewater with the normal sampling techniques in the toplayers of the sediments to a depth of about 30 cm.

Movement of water through the sediments can result in local accumulations in sediment and interstitial water. From earlier research local phosphate accumulations were observed, just below the oxic/anoxic interface at some 0.5-1 cm depth. (Hieltjes, 1980, Kamp Nielsen, 1974 and 1978, Nriagu, 1974, Lung, 1976, Freedman and Canale, 1977, etc.). The mechanism of the phosphate accumulation is often assumed to be the result of simultaneous occurring processes of transport of phosphates, iron and oxygen, the oxygen transport via interstitial water and diffusive transport of oxygen from the overlying water. The oxygen thus keeps the toplayer of the sediments under aerobic conditions. In this environment iron(III)phosphates can precipitate, causing new transport of phosphates -and maybe iron as well- from deeper sediment-layers, resulting in accumulations of iron(III)phosphates. This is consistent with our phosphate accumulations in the toplayers of both lake-sediments.

Unknown components in these processes that need further evaluation are:

(1) the variable accumulation rate
(2) the influence of ortho- and total-phosphate concentration of the infiltrating overlying water
(3) the build up time of the accumulations
(4) is a maximum accumulation (maximum content of the accumulation) reached and if so, at what level. Maybe a maximum is followed by a seep-through, like is the case with a sponge.
(5) the stability of the accumulation at changing redoxconditions
(6) the quantitative effects on phosphorus release are also unknown.

More discussion on phosphates can be found in chapter VII.

10.19 POTASSIUM

Contents and comparison

Potassium contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 66. Some data of lake- and river-sediments from other sources are summarized in table 67.

Table 66.

Potassium-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Potassium Westeinder					
0 - 50	1.2	0.05	0.5	0.3	3.1
0 - 1	1.1	0.06	0.2	0.8	1.7
4 - 6	1.2	0.09	0.3	0.5	1.8
8 - 10	1.3	0.06	0.2	0.9	1.7
25 - 30	1.3	0.15	0.6	0.8	3.1
45 - 50	1.2	0.16	0.7	0.3	3.0
Potassium Elfhoeven					
0 - 50	1.6	0.05	0.4	0.1	2.4
0 - 1	1.5	0.04	0.1	1.3	1.6
4 - 6	1.8	0.08	0.3	1.3	2.2
8 - 10	1.8	0.09	0.3	1.3	2.4
25 - 30	1.5	0.13	0.5	0.6	2.2
45 - 50	1.5	0.17	0.6	0.1	2.4

detection limit = 0.004 % K

Table 67.

Potassium-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry *weight*	% of dry *weight*			
1	1.7	L. Brielle	Hieltjes	1980
0.2	3.0	L. Valencia (Sp.)	Lewis	1981
1.2	2.6	Pek R.	Petrovic	1981
0.061	0.278	Ohio R.	Spencer	1981

Discussion

Potassium occurs in many minerals. The average concentration in the earth crust is 2.1 % K. Potassium is a well-known component of fertilizers. The average value of potassium in lake Elfhoeven (1.6 % K) is about 1.3 times that of Lake Westeinder (1.2 %) in all layers in both sediments. The concentrations slightly increase just below the toplayer and drop back to that level in the layer 45-50 cm again, but the diffences are small. The scatter in the observations is low in the toplayers and increases with depth (table 66). This is twofold: minima become lower with depth, maxima higher. The maximum potassiumcontents of 3.1 and 3.0 % of the dry weight occur at two depths (25-30 cm and 45-50 cm) in the same core in lake Westeinder (core 2). In both lakes the deepest layer contains the lowest amount of potassium, with exeption of cores 2, 16, 17, 22 and 30. In lake Elfhoeven maximum values did occur in all layers deeper than the top few centimeters. The minimum content of potassium was observed in the deepest layer of both sediments.

The potassium contents in both lakebeds were about the same as in other lake- and river-sediments. In lake Brielle, Hieltjes (1980) measured values from 1-1.7 % potassium. In lake Valencia, Lewis (1981) measured 0.2-3.0 % K. The maximumvalues of this study correspond those of river Pek (Petrovic, 1981).

10.20 SELENIUM

The selenium content was below the detection-level of 0.0003 % of the dry weight for all samples in both lake Westeinder and lake Elfhoeven.

10.21 SILICON

Contents and comparison

Silicon contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 68. Some data of lake- and river-sediments from other sources are summarized in table 69.

Discussion

Silicon contents in lake Westeinder and lake Elfhoeven sediments are about the same: 22.6 and 24.9%. Maximum values in the sandy parts of lake Westeinder sediments are about 40%. These maxima are of course higher than the predominantly peaty Elfhoeven sediments that show maximum silicon contents of 31%.

10.22 STRONTIUM

Contents and comparison

Strontium contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 70. Some data of lake- and river-sediments from other sources are summarized in table 71.

Table 68.

Silicon-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Silicon Westeinder					
0 - 50	22.6	0.8	6.7	11.2	41.6
0 - 1	25.0	1.6	6.2	19.4	41.6
4 - 6	23.8	1.8	6.7	13.2	41.3
8 - 10	23.5	1.3	4.9	19.0	36.1
25 - 30	21.7	1.8	7.0	13.4	39.3
45 - 50	19.2	1.8	7.3	11.2	41.1
Silicon Elfhoeven					
0 - 50	24.9	0.6	4.5	9.5	31.0
0 - 1	27.5	0.7	2.3	23.2	30.9
4 - 6	26.6	0.7	2.6	23.2	31.0
8 - 10	26.2	0.6	2.3	23.5	30.1
25 - 30	22.7	1.5	5.4	12.8	30.8
45 - 50	21.8	1.7	6.0	9.5	31.0

detection limit = 0.01 % Si

Table 69.

Silicon-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
20	33	L.Brielle	Hieltjes	1980
6	16	L. Valencia	Lewis	1981

Discussion

The average strontium concentrations in the lakebottoms of lake Westeinder and lake Elfhoeven are about the same: 0.047 and 0.043 %. The average values are very constant with depth. The strontium contents are uniformly distributed over the lake. In lake Elfhoeven sediments the maximum va-

Table 70.

Strontium-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Strontium Westeinder					
0 - 50	0.047	0.001	0.011	0.015	0.072
0 - 1	0.050	0.003	0.012	0.027	0.070
4 - 6	0.049	0.003	0.010	0.034	0.072
8 - 10	0.047	0.003	0.010	0.031	0.068
25 - 30	0.044	*0.003*	*0.011*	*0.018*	*0.059*
45 - 50	0.044	0.003	0.012	0.015	0.061
Strontium Elfhoeven					
0 - 50	0.043	0.001	0.006	0.020	0.066
0 - 1	0.042	0.001	0.002	0.039	0.047
4 - 6	0.041	0.001	0.002	0.037	0.044
8 - 10	0.041	0.001	0.003	0.036	0.044
25 - 30	0.047	0.002	0.008	0.036	0.066
45 - 50	0.045	0.003	0.010	0.020	0.060
detection limit = 0.0004 % Sr					

lues occur in the deeper layers of the lake bottom, in lake Westeinder these maxima are measured in the toplayers. The minimumvalue is measured in the deepest layer in both lakes.

The maximum values of the two lakebottoms are somewhat higher than the values of earlier research: in the Pek river, Petrovic measured the highest value of 0.051 % Sr, which is about 30 % less as the maximum in this study. In Hamburg Port and in Elbe sediments Lichtfuss (1978) measured up to 0.018 % Sr.

10.23 TITANIUM

Contents and comparison

Titanium contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 72. Some data of lake- and river-sediments from other sources are summarized in table 73.

Table 71.

Strontium-contents in lake- and river-sediments

minimum conc. % of dry weight	*maximum* conc. % of dry weight	location	reference	
0.013	0.021	L. Winnipeg (Can)	Allan and Brunskill	1976
0.03	0.038	Alt-Rhein R. (FRG)	Hellmann	1971
0.012	0.018	Elbe R.	Lichtfuss	1978
	0.018	Hamburg Port (FRG)	Lichtfuss	1981
0.009	0.051	R. Pek	Petrovic	1981

Discussion

From table 72, it can be seen that the average titanium concentrations of the sediments of lake Elfhoeven are two times those of lake Westeinder at all depths.
The maximum values occur in the deep layers in lake Westeinder. *The toplayer of lake Elfhoeven sediments contains considerably* more titanium than the deeper layers. This indicates recent inputs. In lake Westeinder, contents below detectionlevel occur quite often in the toplayer of 10 cm thickness, in lake Elfhoeven only in the deepest sedimentlayer. The average contents in all other layers are about the same. The variation of the titaniumcontents in the lake in the deep sediment layers is higher than in the toplayer.

The levels of titanium as measured in the bottomsediments of lake Westeinder and lake Elfhoeven are somewhat lower than those of sediments in other lakes. In lake Brielle-sediments Ti values of 0.2-0.5 % were measured (Hieltjes, 1980). Petrovic detected values of 0.021-0.313 % Ti in sediments of the Danube river. The values that Allan (1975) found in Lake Winnipeg sediments 0.13-0.47 % correspond with Petrovic.

10.24 ZINC

Contents and comparison

Zinc contents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 74. Some data of lake- and river-sediments from other sources are summarized in table 75.

Discussion

The average zinc concentration is 0.021 % in both bottoms. The concentration range is almost the same in the two sediments: 0.0-0.079 % and 0.0-0.081 % for Westeinder and Elfhoeven sediments resp. The toplayers of lake Elfhoeven contain considerably less zinc than all other layers in both lakes. The maximum zinc-content was measured at a depth of 5-15 cm in both lakes. The average values per sediment depth

Table 72.

Titanium-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Titanium Westeinder					
0 - 50	*0.054*	*0.005*	*0.047*	*< det*	*0.252*
0 - 1	0.057	0.010	0.039	< det	0.163
4 - 6	0.048	0.011	0.040	< det	0.127
8 - 10	0.052	0.010	0.039	< det	0.124
25 - 30	0.064	0.015	0.059	0.011	0.252
45 - 50	0.050	0.014	0.058	0.001	0.245
Titanium Elfhoeven					
0 - 50	0.112	0.004	0.032	< det	0.179
0 - 1	0.149	0.008	0.026	0.104	0.179
4 - 6	0.107	0.007	0.025	0.049	0.137
8 - 10	0.104	0.008	0.027	0.056	0.140
25 - 30	0.104	0.007	0.026	0.034	0.139
45 - 50	0.105	0.001	0.037	< det	0.140

detection limit = 0.001 % Ti

Table 73.

Titanium-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference	
% of dry weight	% of dry weight			
0.13	0.47	L. Winnipeg (Can)	Allan	1975
0.2	0.5	L. Brielle	Hieltjes	1980
0.021	0.313	Danube R.	Petrovic	1981

are about the same for the two lakebottoms, but especially in lake Westeinder, the zincconcentrations vary considerably in horizontal direction.

Table 74.

Zinc-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. mean	stand. deviat. sample	min. value	max. value
cm	% of the dry weight				
Zinc Westeinder					
0 - 50	0.021	0.002	0.018	< det	0.079
0 - 1	0.017	0.006	0.022	< det	0.061
4 - 6	0.020	0.004	0.016	< det	0.062
8 - 10	0.028	0.006	0.023	< det	0.079
25 - 30	0.021	0.003	0.013	0.008	0.054
45 - 50	0.017	0.003	0.012	< det	0.047
Zinc Elfhoeven					
0 - 50	0.021	0.002	0.014	< det	0.081
0 - 1	0.005	0.002	0.006	< det	0.015
4 - 6	0.028	0.002	0.008	0.013	0.040
8 - 10	0.027	0.002	0.009	0.010	0.041
25 - 30	0.024	0.005	0.019	0.009	0.081
45 - 50	0.020	0.003	0.011	0.007	0.045

detection limit = 0.001 % Zn

The average concentration of zinc in the toplayer of lake Elfhoeven is far smaller than at all other depths in both lakes. In this layer in lake Elfhoeven all contents are low, as can be seen in table 74. The same was observed with lead in the toplayer of the sediments. This is in contrast to the high average titanium content in the toplayer of lake Elfhoeven sediments (table 72) and especially to the high coppercontents in the toplayers of both lakes (table 46).

The zinc concentrations, measured in the sediments of some Canadian lakes (Nriagu, 1982) are like those, measured by us. Most other sediments contain less zinc, as can be seen from table 75. Zinc contents of soils in the Netherlands, *0.001-0.01 % Zn, as reported by Eysakkers (1981) are lower* than measured in this study. Industrial activities can be the source for the very high contents, measured in the port of Hamburg (Lichtfuss, 1981) and in the river Drau (Teherani, 1981). Iskandar reported zinccontents of 10 lakes in Wisconsin (USA). Minimum zinccontents in the study of Iskandar and Keeney occur mainly in the deepest sediment layers (in 7 lakes out of 10: 70 %). We found minimum zinccontents mainly in the toplayers of the sediments: in lake Westeinder 9 times in 17 cores (53 %) and in lake Elfhoeven

Table 75.

Zinc-contents in lake- and river-sediments

minimum conc.	maximum conc.	location	reference
% of dry weight	% of dry weight		
0.007	0.016	Rhone R.	Addad 1980
0.0086	0.0242	L. Winnipeg (Can)	Allan and Brunskill 1977
0.0025	0.039	Seine (France)	Boust 1981
0.0025	0.0236	Gulf of Catania (Italy, marine)	Castragna 1982
0.0061	0.099	Stephens Creek Res. (Austral.)	Coggins 1979
0.0016	0.0025	Spencer Gulf (Australia)	Dossis 1981
0.0020	0.0285	L. Marker	Ente 1981a
0.0001	0.011	Dutch soils	Eysakkers 1981
	0.0118	L. Windermere	Hamilton-Taylor 1979
0.0012	0.0195	L. Wisconsin (USA)	Iskandar 1974
0.0021	0.01	Casco Bay (USA)	Larsen 1983
	0.24	Hamburg Port (FRG)	Lichtfuss 1981
0.0016	0.0079	Bermuda (marine)	Lyons 1983
0.030	0.085	L. Kelly	Nriagu 1982 *
0.0125	0.040	L. Lohi	Nriagu 1982 *
0.008	0.040	L. Nelson	Nriagu 1982 *
	0.012	Lough Neagh	Rippey 1982
0.008	0.024	Rhine R.	Schleichert 1975
0.0063	0.0226	Ohio R.	Spencer 1981
0.016	0.74	R. Drau	Teherani 1981

* These lakes are situated within 30 km from the smelters of Sudbury, Ontario, Canada.

9 times in 13 cores (70 %). This suggests decreasing discharges *as was also the case with lead.*

10.25 WATERCONTENTS

Contents and comparison

Watercontents in the sediments of lake Westeinder and lake Elfhoeven are shown in table 76.

Discussion

The watercontent in lake Westeinder sediments and lake Elfhoeven sediments are both very high down till 50 cm depth. The average content of all samples is 84.4 % and 83.8 % resp. The toplayers have very high watercontents (91.4 % and 93.0 % resp.) as could be expected in our shallow lakes. The watercontent remained high on all depths in the sediments.

Table 76.

Water-contents in the lake-sediments

layer thickness	aver. content	stand. deviat. *mean*	stand. deviat. *sample*	min. value	max. value
cm	% of the dry weight				
Watercontent Westeinder					
0 - 50	84.4	1.4	12.7	32.7	99.1
0 - 1	91.4	3.0	12.2	55.5	99.1
4 - 6	82.1	3.6	14.7	32.7	95.5
8 - 10	81.8	3.3	13.7	37.8	94.8
25 - 30	82.7	2.6	10.7	54.4	92.9
45 - 50	83.9	2.5	10.0	54.4	92.9
Watercontent Elfhoeven					
0 - 50	83.8	1.0	7.9	64.9	98.8
0 - 1	93.0	1.2	4.4	83.5	98.5
4 - 6	81.4	2.1	7.4	66.5	93.2
8 - 10	79.4	1.6	6.0	68.6	89.1
25 - 30	82.3	2.0	7.2	65.1	91.4
45 - 50	82.6	2.0	7.1	64.9	93.9

In the 45-50 cm layer the water content still was 83.9 and 82.6 % in the two sediments. This was already clear during the sampling: the cores had to be handled very carefully during exchange of the liners in the sampling apparatus and during transport.

Frape (1981) measured watercontents of 85-90 % constant over the upper 2 m in coarse brown, filamentous peat in Perch lake (Canada). The same type of soil encountered several times in lake Westeinder and almost everywhere in lake Elfhoeven.
From lake Brielle some cores were obtained (length 0.12 m). In spite of the high organic content of this sediment the watercontent fell down rapidly from 90 to 65 % (Hieltjes, 1980). To what depths the high watercontents and the corresponding loose structure of the sediments in lake Westein*der and Elfhoeven prevail is not known. Our qualitative ob*servations down to 90 cm did not indicate decreasing watercontents: the sediment remained very thin, demandig the utmost care in handling and transporting. This is consistent with Lewis, who measured high water contents in lake Valencia (Lewis, 1981). The contents remained about constant on 80 % till a depth of 1 m and next fell to 70 % between 1 m *and about 5 m.*

10.26 AMOUNT OF EACH ELEMENT IN THE 50 CM THICK SEDIMENTLAYER

Table 77 shows the total amounts of all elements in the entire sediment layer with a thickness of 50 cm. Calculation is done as follows. With

W	= *watercontent of the sediment*	[%]
A	= surface of the sediment	[sqm]
d	= thickness of the sedimentlayer	[m]
ro	= mass density of the sediment	[tons * m(-3)]
E	= concentration of the element	[% of the dry weight]
G	= total amount in the layer	[tons element E]

the lakebed contains A * d * ro * (100 - W)/100 [tons dry sediment]
This results in a quantity of the element E, G(E) of:

G(E)=(100 - W) * A * d * ro * E * 10(**-4) [tons element E]

remarks

- sedimentsurface is assumed equal with watersurface A.
- thickness of the sedimentlayer is considered 0.5 m
- mass desity (dry material) is assumed 2.5 tons*m(-3).

Using the average data the total amounts become:

Lake Westeinder G = 18135 * E [tons of element E]
Lake Elfhoeven G = 2227.5 * E [tons of element E]

The calculated average concentrations and total amounts are shown in table 77.

Discussion

The average watercontent of both sediments is very high down to 50 cm depth and nearly identical in both lakes.
The elements can roughly be divided in three groups whether their concentrations in lake Westeinder are higher, about equal or less than in lake Elfhoeven. The groups are:
(1) The average contents of Cr, Hg, P, Se, Si, Sr and Zn in both lake sedimecontents differ by a factor 0.8 to 1.25 to those of lake Elfhoeven sediments.
(2) The average contents of Ca, Cu and Mn of the lake Westeinder sediments are 25 % or more larger (up to a factor 4.2 for OPO4-P in the interstitial water) than the average contents of those elements in lake Elfhoeven.
(3) The average contents of Al, As, Co, Fe, K, Mg, Ni, Pb and Ti in lake Elfhoeven sediments are 25 % or more larger than those in the lake Westeinder sediments. Especially for As, Ni, Pb and Ti the conclusion can be drawn that lake Elfhoeven sediments are more polluted with arsenic and these heavy metals than lake Westeinder sediments.
We do not know the causes for these differences. One of the sources for species in both lake sediments is Rhinewater, but this influence can not explain the measured differences. The differences in composition of sediments must also be due to discharges on the lakes or rivers and boezemwaters, that supply water to the lakes. Different concentration mechanisms can than be the cause for the observed differences than.

Table 77.

Amount of elements in lake Westeinder and Elfhoeven sediments

Average concentrations and total amounts of 20 elements in the 50 cm thick toplayer of lake Westeinder and lake Elfhoeven sediments

	lake Westeinder		lake Elfhoeven	
	average concentr.	total amount	average concentr.	total amount
Sediment				
Al	0.9 %	16322 tons Al	2.1 %	4678 tons Al
As	0.002 %	36.3 tons As	0.003 %	6.7 tons As
Ca	11.6 %	210366 tons Ca	7.9 %	17597 tons Ca
Cr	0.023 %	417 tons Cr	0.027 %	60.1 tons Cr
Co	0.003 %	54.4 tons Co	0.005 %	11.1 tons Co
Cu	0.014 %	254 tons Cu	0.010 %	22.3 tons Cu
Fe	2.45 %	44931 tons Fe	3.39 %	7551 tons Fe
K	1.2 %	21762 tons K	1.6 %	3564 tons K
Mg	0.08 %	1632 tons Mg	0.23 %	512 tons Mg
Mn	0.21 %	3990 tons Mn	0.11 %	245 tons Mn
Ni	0.002 %	36.3 tons Ni	0.003 %	6.7 tons Ni
P	0.082 %	1487 tons P	0.084 %	188 tons P
Pb	0.01 %	181 tons Pb	0.02 %	46.8 tons Pb
Si	22.6 %	409851 tons Si	25.0 %	55688 tons Si
Sr	0.047 %	853 tons Sr	0.043 %	95.8 tons Sr
Ti	0.05 %	907 tons Ti	0.11 %	245 tons Ti
Zn	0.021 %	381 tons Zn	0.021 %	46.8 tons Zn
Interstitial water				
oPO4	2.08 ppm P	8.2 tons P	0.50 ppm P	0.2 tons P
tP	3.27 ppm P	12.8 tons P	1.11 ppm P	0.5 tons P
Watercontent				
	84.4 % H2O		83.8 % H2O	

The phosphate concentrations (ortho-P and total-P) of the interstitial water of the sediments in lake Westeinder are three- to fourfold those of lake Elfhoeven.

10.26.1 The composition related to other sediments

The solid earth crust is composed of the major elements oxygen: 46.6 %, silicon: 27.72 %, aluminum: 8.13 %, iron: 5.0 %, calcium: 3.63 %, sodium: 2.83 %, potassium: 2.59 %, magnesium: 2.09 % and titanium: 0.44 % (% of dry weight).

The solid earth crust further contains 0.14 % H, 0.1 % Mn, 0.12 % P and 0.001 to 0.01 % of the elements S, C, Cl, Rb, F, Sr, Ba, Zr, Cr, V and Zn. The part of the other elements in the earth crust is less (Mason, 1952)

Average values of some inorganic compounds in sediment are given by Weast (1982): SiO_2: 57.95 %, TiO_2: 0.97 %, Al_2O_3: 13.39 %, Fe_2O_3: 3.47 %, FeO: 2.08 %, MgO: 2.65 % and CaO: 5.89 %. Similar values are given by Cowgill (1977) with exeptions for the higher aluminum and iron contents in the lake sediments of Linsley pond (USA). The calculated percentages SiO_2 of lake Westeinder and lake Elfhoeven sediments, 48.28 % and 53.31 % resp. are somewhat lower. As the silicon contents vary from 11.21-41.63 % Si and from 9.48-31.02 % resp. in the two lakes the calculated SiO_2 contents vary from 24.0-89.1 % and from 20.3-66.4 % resp., the high values being sandy sediments.

The sediments can be assumed to consist of SiO_2, $CaCO_3$, clay and FeOOH. The total percentage of compounds and elements of table 77 is now calculated. The relatively low concentrations of all other elements are added.

$$\frac{M(SiO_2)}{M(Si)} * [Si] + \frac{M(CaCO_3)}{M(Ca)} * [Ca] + \frac{M(FeOOH)}{M(Fe)} * [Fe] +$$

+ the sum of the other elements

with M = molecular weight of the element or compound and the relevant data this results in a total % (dry weight) of the measured elements of

$$2.14 * [Si] + 2.50 [Ca] + 1.59 [Fe] + \text{sum other elements}$$

In lake Westeinder application of this rough model with percentages for SiO_2, $CaCO_3$, FeOOH and sum of other elements of resp. 48.3 %, 29.1 %, 3.9 % and about 2.5 % results in a total percentage of dry material of about 84 %. In lake Elfhoeven these percentages are 53.3, 19.6, 5.4 and about 4.5 %, the sumpercentage becomes 83 %. The other 16 and 17 % can be considered to be mainly oxygen, sodium and some chlorine and sulfur. The rest of the elements were not measured: they will be minor elements.

Chapter XI

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Curriculum Vitae

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